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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1110

Part of Journal of Research of the National Bureau of Standards, Volume 21, July 1938

PRESSURE LOSSES FOR FLUID FLOW IN 90° PIPE BENDS

By K. Hilding Beij.

ABSTRACT

Pressure losses were determined for nine 4-inch steel, 90° pipe bends of radii from 6 to 80 inches. The results are discussed in relation to those found by previous investigators under comparable test conditions. For bends having radii of four pipe diameters or less, all the results which are discussed may be correlated on the basis of pipe roughness. Further data are needed to establish a working formula. No correlation could be obtained for the bends of larger radii. For such bends the maximum published values should be used in engineering work until more comprehensive data become available.

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I. INTRODUCTION

1. PURPOSE OF WORK

The 90° pipe bend is perhaps the most frequently used fitting in piping systems. The pressure losses in such bends are therefore of considerable engineering importance. However, although many investigators have studied the problem, the results which they have obtained have not been satisfactorily correlated. The work discussed in this paper was undertaken to obtain information which would assist in the correlation of previous results, and further, to furnish data for engineering use. This work forms part of an extended study of pipe bends in progress at the National Hydraulic Laboratory, another part of which has already been published [1].[1]

[1] Figures in brackets refer to the literature references at the end of this paper.

2. STATEMENT OF PROBLEM

In this paper the term *pipe bend* will be restricted to pipes of circular cross section bent to the form of circular arcs. A bend will always be considered with relation to the straight pipes connected to its two ends. These straight pipes, or *tangents*, are *long;* that is, whatever the velocity distribution may be at the upstream end, the length is sufficient for the gradual modification of the distribution until it assumes a characteristic form which remains unchanged for the remainder of the pipe. Thus, at the entrance to the bend the velocity distribution will be the characteristic distribution for straight pipe. At the downstream end of the bend the velocity distribution depends on the nature of the flow in the bend. This distribution changes gradually in the downstream tangent until it assumes the form characteristic of straight pipe. It is found that in the bend and in the downstream tangent, the pressure losses are greater than in equal lengths of straight pipe with characteristic velocity distribution.

The conventional manner of expressing the excess pressure losses in the bends and downstream tangents will be adopted. According to this view, we assume that the total loss in a bend with long tangents is the sum of the loss which would occur with characteristic velocity distribution in straight pipe of the same axial length, plus an excess loss in the bend, plus an excess loss in the downstream tangent. That is, measuring pressure losses between a point on the upstream and a point on the downstream tangent, at each of which characteristic velocity distribution for straight pipe prevails, we find

$$P/\gamma = H = H_S + H_B + H_T, \tag{1}$$

or putting

$$H_B = \zeta \frac{U^2}{2g}, \tag{2}$$

$$H_T = \theta \frac{U^2}{2g}, \text{ and} \tag{3}$$

$$H_S = \lambda_S \frac{l}{d} \frac{U^2}{2g}, \tag{4}$$

we have

$$\frac{P}{\gamma} = H = \lambda_S \frac{l}{d} \frac{U^2}{2g} + \zeta \frac{U^2}{2g} + \theta \frac{U^2}{2g}, \tag{5}$$

where

P = the total pressure loss,
γ = the specific weight of the fluid,
H = the total head loss (measured as the height of a column of the same fluid as that flowing in the pipe line),
H_S = the head loss with characteristic velocity distribution in a straight pipe of axial length equal to the distance between the points of pressure measurement,
H_B = the excess head loss in the bend,
H_T = the excess head loss in the downstream tangent,
U = the mean velocity, which is the quantity of flow, Q, divided by the cross-sectional area of the pipe, A,
g = the acceleration of gravity,
λ_S = the coefficient of resistance for straight pipe with characteristic velocity distribution,

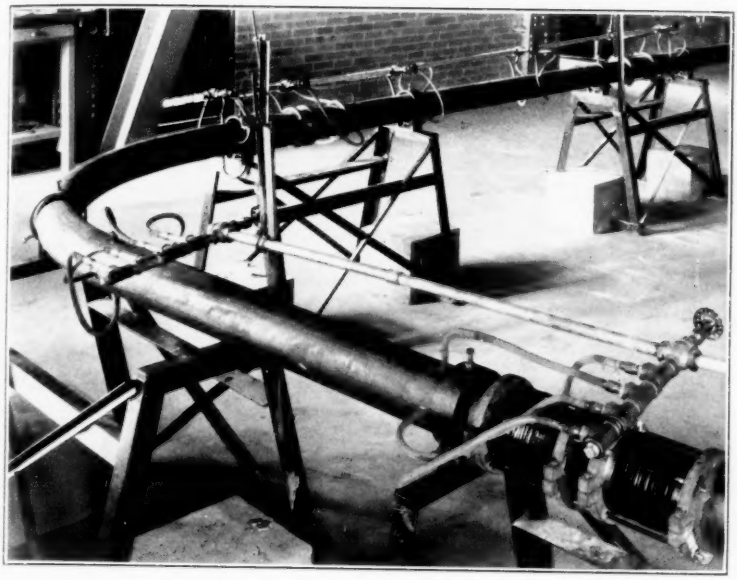

FIGURE 1.—*Pipe bend of long radius as set up for test.*

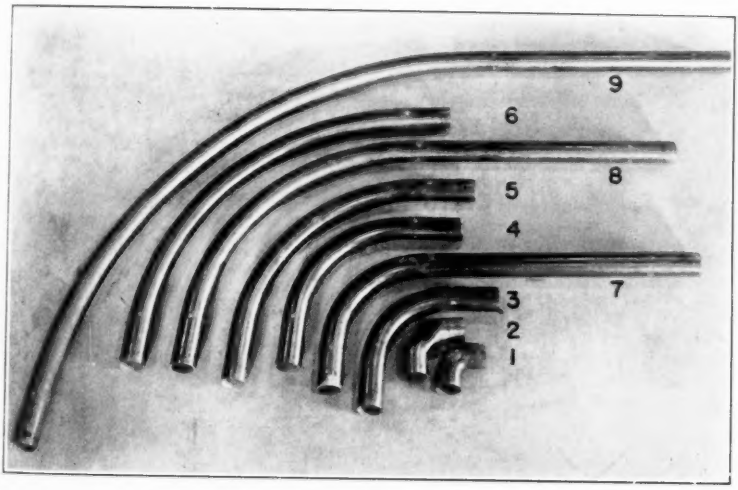

FIGURE 2.—*Pipe bends which were tested.*

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l=the length of pipe,
d=the diameter of the pipe,
ζ=the deflection coefficient, and
θ=the tangent coefficient.

We may also write

$$H=H_s+\eta\frac{U^2}{2g}, \tag{6}$$

where

$$\eta=\zeta+\theta \tag{7}$$

is the bend coefficient.

It is tacitly assumed in these equations that the interior surfaces of the bend and the tangents are the same, the cross section does not vary, and no disturbing influences such as rough joints are present.

The coefficients η, ζ, and θ are, in general, functions of the dimensions and roughness of the pipe and bends, and the Reynolds number. The immediate problem is to determine these functions for 90° pipe bends.

3. PREVIOUS WORK

It is unnecessary to repeat here all previous results, since in many cases the published data are insufficient for the purpose of comparison, or the test conditions are not comparable with those of the present work. Therefore, only a few representative results have been selected either for direct comparison or to illustrate some particular point. See figures 8, 11, and 12. It must be emphasized that the results given in the figures represent the best which have been obtained, and that the discrepancies are far too large to be accounted for by experimental errors alone.

II. PIPES AND BENDS

Steel tubing of nominal 4-inch internal diameter, in lengths of 7 to 8 feet, was used. Internal diameters were measured with a pipe gage about 6 inches from each end of each pipe and on four diameters at about 45° spacing. The mean of all measurements was 10.23 cm and the maximum deviation from the mean was 0.03 cm.

At the joints the pipes were simply butted together and held in place by friction clamps around the pipe connected by bolts. The joint was made watertight by a wrapping of rubber tape laid in gasket shellac and covered by a layer of friction tape. To make the joints match perfectly, each pipe end was machined. The pipe was centered as truly as possible in a lathe, the end cut off square, and the outer surface machined back for a few inches from the end to a predetermined diameter. Finally, a finishing cut on a 0.5° taper (half-angle) was made on the inside until the inside diameter at the very end was a certain predetermined value. The change in diameter due to this tapering cut was in no case as great as 0.2 cm.

Similar joints were used on all the smaller bends. On those which were too large to be mounted in a lathe, a simplified joint was added. A piece about 9 inches long was cut from each end of the bend by a band saw, and matchmarked so that it could be returned to its original position. Burrs were removed by filing. The other end of each of these short pieces was then machined to match the straight pipe ends.

The joints which were made by sawing matched practically as well as those which were machined, but they were more difficult to assemble and to make watertight.

The pipes and bends were supported in clamping rings mounted on steel stands. The clamping screws were used to make final adjustments of the pipe to line and grade. Figure 1 shows one of the larger bends set up for test.

The bends are shown in figure 2. The two smallest (numbers 1 and 2) were standard seamless welding fittings to which short tangents were welded. The inside surfaces of the welds were ground true. All of the other bends were made of the same steel tubing as the straight pipes, bent to the desired dimensions. All had short integral tangents at both ends except three (numbers 7, 8, and 9) which had tangents approximately 4 feet long on the upstream ends.

III. APPARATUS

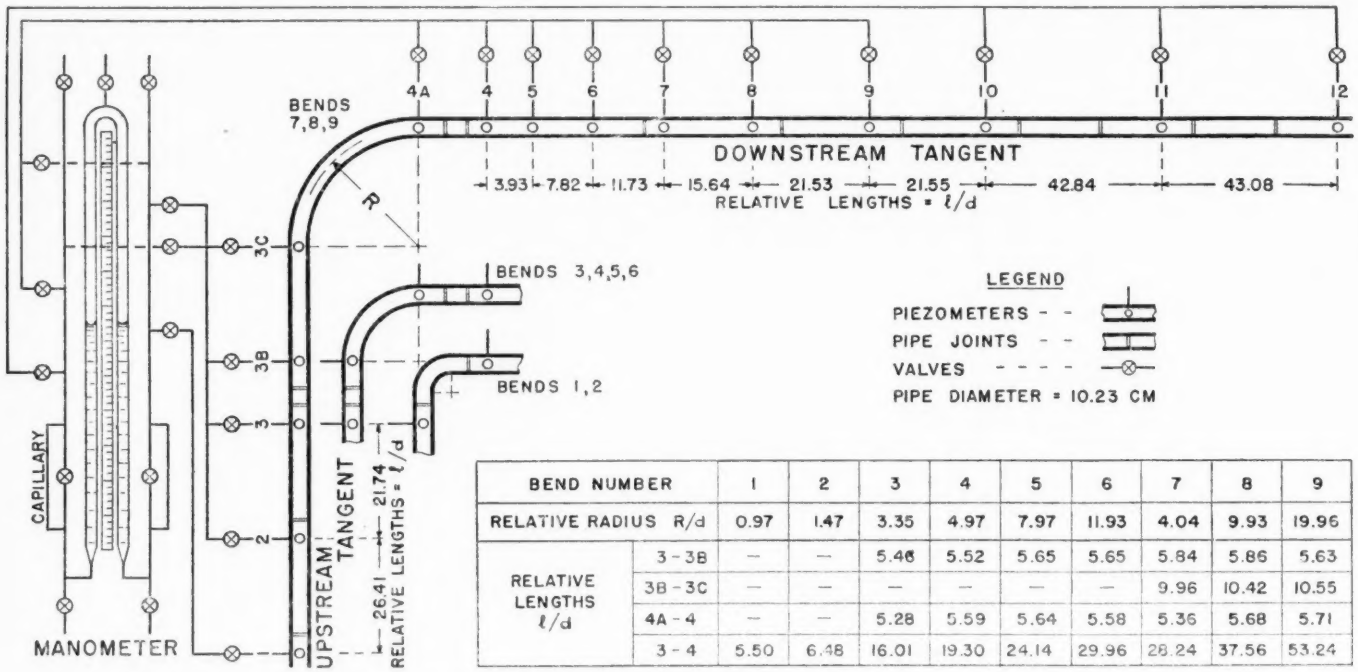
A diagram of the pipe line and the manometer connections is given in figure 3. A differential air-water manometer consisting of two glass tubes of about 23 mm bore was used for measuring pressure differences. With this size of tubing no meniscus difficulties were encountered. Water levels in the tubes were read with a cathetometer against a scale set between the manometer tubes. The scale was graduated in millimeters, and tenths of millimeters were estimated. To damp out excessive oscillations at the higher velocities, capillary tubes of 1-mm bore, about 6 inches long, were connected into the pressure lines. The damping was adjusted so that the oscillations were never completely eliminated.

Each piezometer connection at the pipes consisted of four holes, 4 mm in diameter, drilled at 90° intervals in the circumference. These were connected to a manifold and, through a valve, to the header leading to the manometer. Valves and drains were provided for flushing air from all pressure lines. It will be noted from the diagram in figure 3 that in most cases the pressure difference between two adjacent piezometers on the pipe was obtainable only by taking the difference of two readings. For example, to obtain the pressure difference between piezometers 5 and 6, it was necessary to subtract the measured difference between 1 and 5 from that between 1 and 6.

Water was supplied from a constant-level tank through a stilling tank and several lengths of straight pipe upstream from the first piezometer connection. The flow was controlled by a valve at the discharge end of the line.

The discharge was caught and measured in weighing tanks. Times were measured by stop watch. The time intervals and amounts weighed were adjusted according to the flow to obtain a minimum precision of 1 part in 2000. There was no difficulty in holding the flow constant to 1 part in 1000.

Temperatures were measured to the nearest tenth of a degree centigrade by a calibrated mercury thermometer set into the pipe near the discharge end.



BEND NUMBER		1	2	3	4	5	6	7	8	9
RELATIVE RADIUS R/d		0.97	1.47	3.35	4.97	7.97	11.93	4.04	9.93	19.96
RELATIVE LENGTHS ℓ/d	3 - 3B	—	—	5.46	5.52	5.65	5.65	5.84	5.86	5.63
	3B - 3C	—	—	—	—	—	—	9.96	10.42	10.55
	4A - 4	—	—	5.28	5.59	5.64	5.58	5.36	5.68	5.71
	3 - 4	5.50	6.48	16.01	19.30	24.14	29.96	28.24	37.56	53.24

FIGURE 3.—*Diagram of pipe and bend as set up for testing, showing location of pipe joints, piezometers, and arrangement of pressure connections to manometer.*

IV. EXPERIMENTAL RESULTS

1. RESISTANCE COEFFICIENTS FOR STRAIGHT PIPE

In each test, pressure differences were determined, directly or by difference, for each section of pipe between the piezometers. It was evident from inspection of the results for the downstream sections that in every case the effects due to the presence of the bend were undetectable beyond piezometer 7. (See fig. 3.) For convenience, the section between piezometers 7 and 9 was used to establish the resistance coefficient for straight pipe, and the remaining downstream sections were not further used. The resistance coefficients for section 7 to 9 are given in figure 4 as functions of Reynolds number.

The results for sections 1 to 2 and 2 to 3, upstream from the bend, were compared with those for the section from 7 to 9, to determine whether the upstream tangent was of sufficient length. The data for section 2 to 3, immediately upstream from the bend, were in good agreement with those for section 7 to 9. Therefore, it was concluded that characteristic velocity distribution was established in section 2 to 3, and hence at the entrance to the bend.

In all cases bend losses were determined from the data for the section 3 to 7. For the lengths of straight pipe in this section, the resistance coefficient for straight pipe with characteristic velocity distribution was taken as that determined for section 7 to 9. (See fig. 4.) For the length of pipe containing the bend, the resistance coefficient for characteristic velocity distribution in straight pipe was determined as explained below.

Preliminary measurements with bend 1 in place showed that the pressure loss was rapidly increasing owing to rusting of the pipes. Check measurements were made at intervals until the resistance coefficients showed practically no change over a period of about 2 weeks. Then the test runs were made. As the bend was in place during all this time, it was considered to have rusted to the same degree of roughness as the straight pipe. Insofar as could be determined by inspection after the tests were completed, this appeared to be the case. The resistance coefficient for the section of pipe containing the bend was therefore assumed to be the same as for the straight pipe.

Before bend 2 was tested, the pipeline was taken down and all loose rust scraped out with a wire brush. Again the first few runs, with bend 2 in place, showed rapid change in resistance. After a week or two the change was very slow and the tests were run. However, the bend itself did not rust quite as much as the pipe.

The same procedure was carried out for bends 3 to 6, inclusive. For bend 4, the pipe was cleaned more thoroughly, and the resistance of the straight pipe at the time of testing was, in general, somewhat lower than for any of the other tests. This lowest value of the resistance coefficient was used as the value pertaining to the section of pipe containing the bends, 2 to 6 inclusive. It is believed that this assumption is very nearly true, as inspection showed these bends to be rougher than new pipe but not as rough as bend 1. In any case the resulting errors are not large. If, for example, the assumed straight pipe coefficient for bend 6 (the worst case) is 5 percent in error, then the bend coefficient will be 5 percent in error.

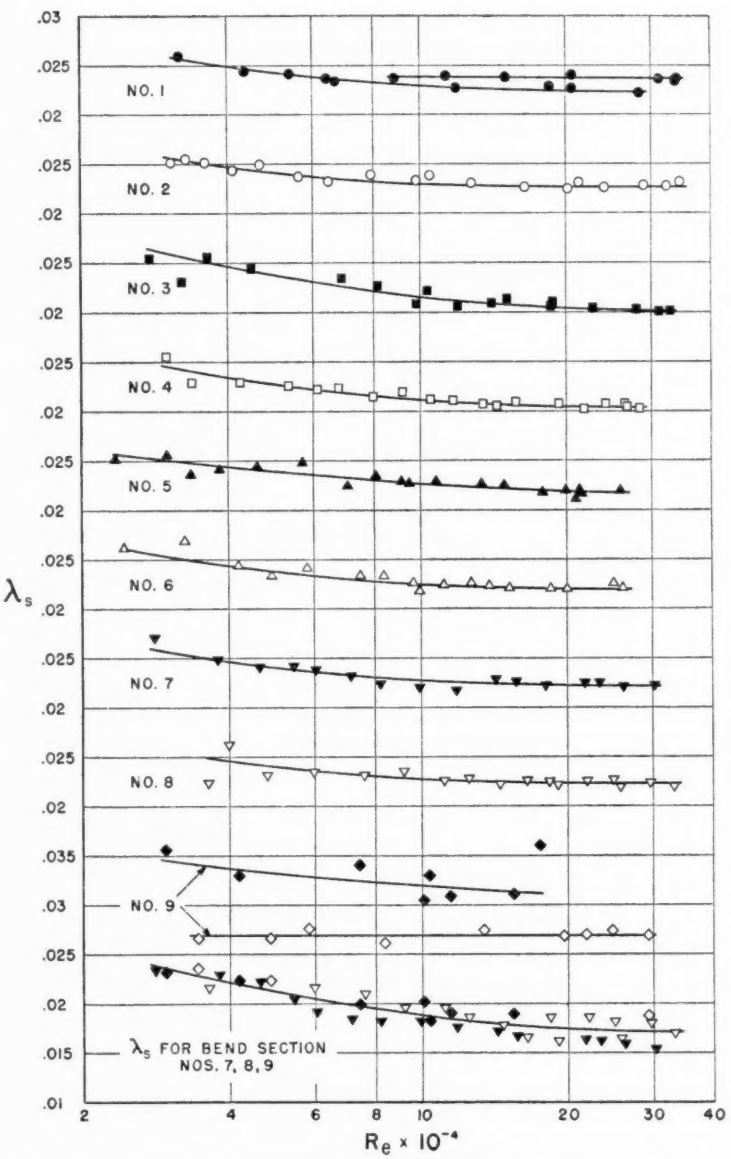


FIGURE 4.—*Resistance coefficients for straight pipe as functions of Reynolds number.*

The numbered curves give the resistance coefficients found in the pipe section between piezometers 7 and 9 during tests on the bends of corresponding number. The two curves for No. 9 correspond to the two groups of tests on this bend. The lowest curve represents the resistance coefficients found for the short integral upstream tangents on bends 7, 8, and 9.

The purpose of the long integral tangents on bends 7, 8, and 9 was to provide for an independent measurement of the resistance coefficient in these bends. The results, given by the lowest curve in figure 4, were rather rough on account of the relatively short lengths available,

but agreed well with the initial measurements on the new straight pipe. As these bends rusted hardly at all, the average of the results on the tangents was used for the section of pipe containing these bends.

It will be noted from figure 4 that the resistance coefficients for straight pipe are approximately the same for all tests except those with bend 9. In this case the pipes were not cleaned before the tests and thus the friction coefficients were considerably higher. Also the friction coefficients for the first half of the tests on this bend differed from those of the second half, as indicated by the two curves. However, the average bend coefficients were practically the same in each case. Until the effect of roughness is better understood, the results for this bend must be considered as not strictly comparable with those for the other bends.

2. BEND COEFFICIENTS

The bend coefficients, as defined by the relation

$$H=H_s+\eta\frac{U^2}{2g} \tag{6}$$

are plotted in figures 5 and 6 as functions of the Reynolds number. It appears that, in general, the coefficients are independent of Reynolds number within the range of the tests, although those for bend 6 and, to a slighter extent, those for bend 7, increase with increasing Reynolds

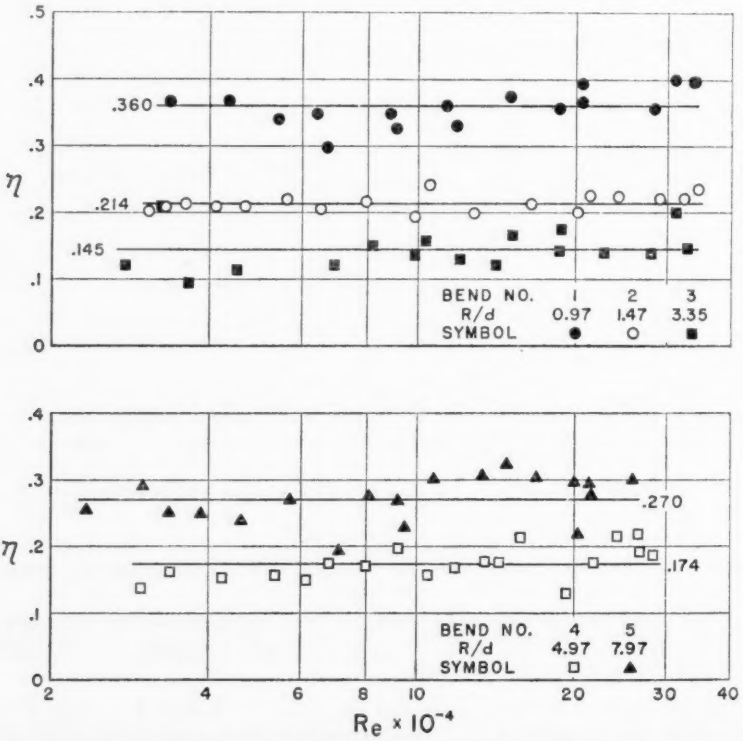


FIGURE 5.—*Bend coefficients as functions of Reynolds number.*

See also figure 6.

numbers. However, since the increase may very likely be due to experimental errors, the average values indicated in the figures by the heavy horizontal lines are taken to represent the results.

The average values are listed in table 1 and are plotted in figure 7 as a function of the relative radius of the bends. The *relative radius* is the ratio of the bend radius, R, to the pipe diameter, d. With the

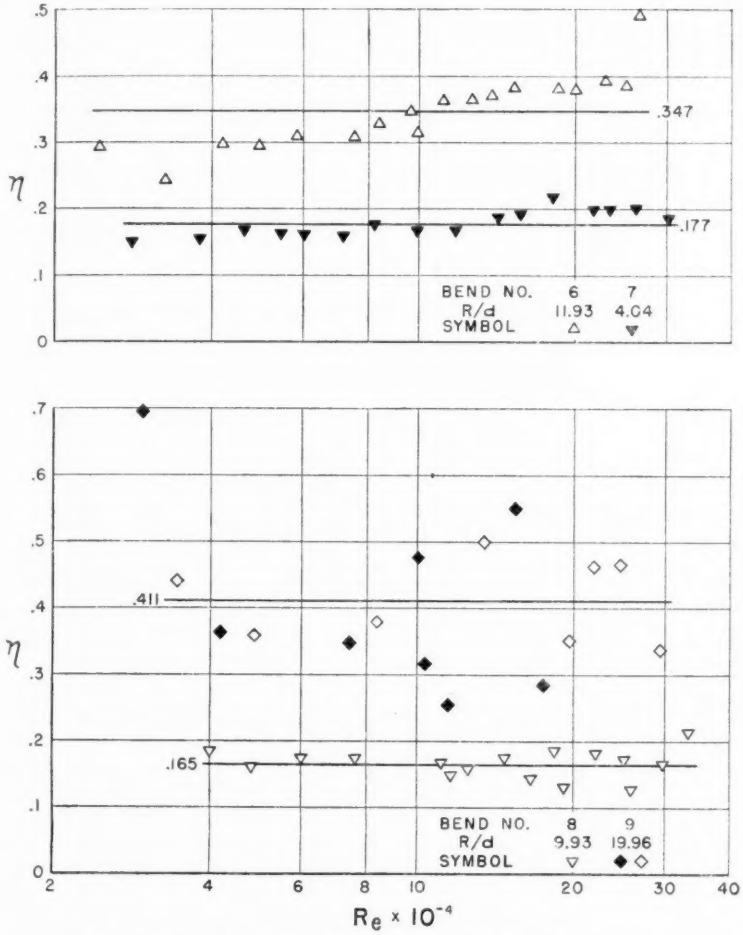


FIGURE 6.—*Bend coefficients as functions of Reynolds number.*

See also figure 5.

exception of the value for bend 8, the points are well represented by the smooth curve drawn in the figure. The reasons for ignoring the value for bend 8 in drawing the curve will be given later.

In figure 8, the heavy line represents the curve of figure 7, and the other curves the results of Hofmann [2], Davis [3], Balch [4], Vogel [5], and Brightmore [6]. It is evident that the quantitative agreement is not good. Even with due allowance for experimental errors (which are bound to be large from the nature of the problem), it

appears that variables other than Reynolds number and relative radius are entering.

Qualitatively there is some agreement in that the curves indicate

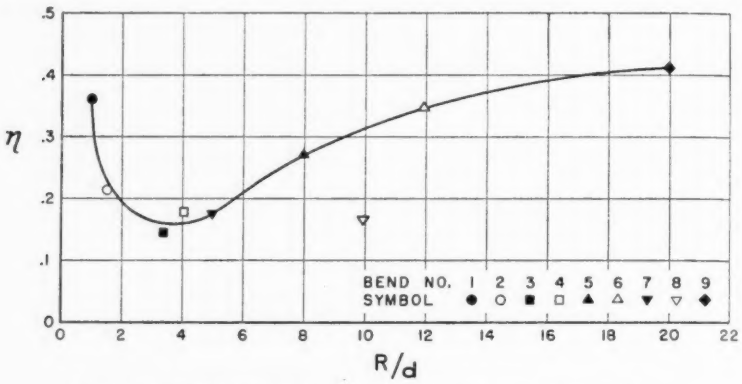


FIGURE 7.—*Bend coefficients as functions of the relative radius.*

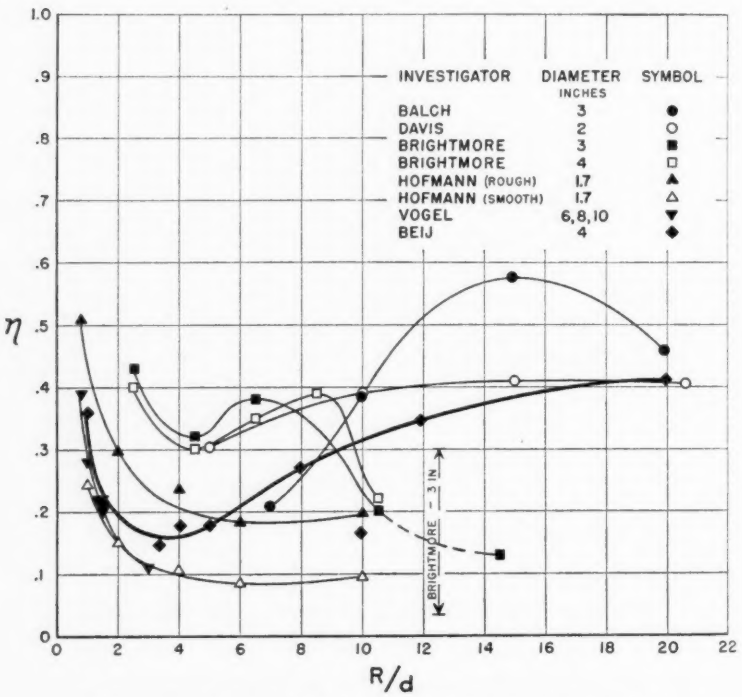


FIGURE 8.—*Bend coefficients found by various investigators.*

The heavy curve is the curve of figure 7 representing the results of the present investigation.

two regions of flow. For the lowest relative radii the coefficient decreases rapidly to a minimum in the neighborhood of $R/d=5$. Then there is a gradual rise to an apparent maximum somewhere near the value $R/d=15$. Finally, as the relative radius gets very

large there is probably a third region in which the coefficient decreases—presumably approaching zero as the relative radius approaches infinity.

TABLE 1.—*Results of tests on 90° pipe bends—4-inch steel pipe*

[Actual inside diameter, $d=10.23$ cm]

Bend	Relative radius R/d	Bend coefficient η	$(\lambda_0-\lambda_s)$	$\frac{1}{a}$	$\frac{1}{\beta}$	Tangent coefficient θ	Deflection coefficient ζ
1	0.97	0.360	0.0155	32	32	0.18	0.18
2	1.47	.214	.0155	32	32	.18	.03
3	3.35	.145	.0155	32	32	.18	−.03
4	4.97	.174	.0155	32	32	.18	−.01
5	7.97	.270	.0155	32	32	.18	.09
6	11.93	.347	.008	32	32	.09	.26
7	4.04	.178	.0155	32	32	.18	.00
8	9.93	.165	.008	32	32	.09	.08
9	19.96	.411	.0155	32	32	.18	.23

3. TANGENT COEFFICIENTS

The tangent coefficient is defined by the relation

$$H_T=\theta\frac{U^2}{2g}, \tag{3}$$

where H_T is the difference between the total head loss in the tangent and the head loss which would occur in an equal length of straight pipe with characteristic velocity distribution. Ideally, the head loss should be measured between the downstream end of the bend and some point on the tangent slightly downstream from the point where effects of the bend have disappeared. This was attempted, but it was found that accurate pressures could not be measured at the downstream end of the bend. It is believed that the disturbed flow and the rusting near or at the piezometer openings were the causes of the inconsistent pressure indications. In general, however, the measurements at piezometer 4 (fig. 3) appeared to be reliable except for a few cases. Hence, the available data consist of the head losses for the three tangent sections 4 to 5, 5 to 6, and 6 to 7, respectively.

For any point of the tangent we define a resistance coefficient λ_z by the relation

$$\frac{dh}{dz}=\lambda_z\frac{1}{d}\frac{U^2}{2g}, \tag{8}$$

where dh/dz is the head-loss gradient along the tangent and z is measured downstream from the end of the bend.

Then for a tangent section between the points $z=a$ and $z=b$, we have by integration of eq 8

$$H_{ab}=h_a-h_b=\bar{\lambda}_z\left(\frac{b-a}{d}\right)\frac{U^2}{2g}, \tag{9}$$

where $\bar{\lambda}_z$ is the mean resistance coefficient for the section. This mean coefficient was computed from the experimental data for each of the

three sections of the downstream tangent for each bend. The results showed no variation with Reynolds number, within the limits of experimental accuracy.

From these experimentally determined mean coefficients it is necessary to derive λ_z as a function of z. This function may then be integrated for the complete tangent in order to arrive at values of the excess head loss, H_T, and the tangent coefficient, θ. As the precision of the measurements is not great, a first approximation fulfilling the following conditions will suffice:

1. The function $\lambda_z=f(z)$ must agree with the experimental results for the mean coefficients $\bar{\lambda}_z$.

2. The function must start at some maximum value λ_0 at the end of the bend where $z=0$, and decrease continuously, approaching

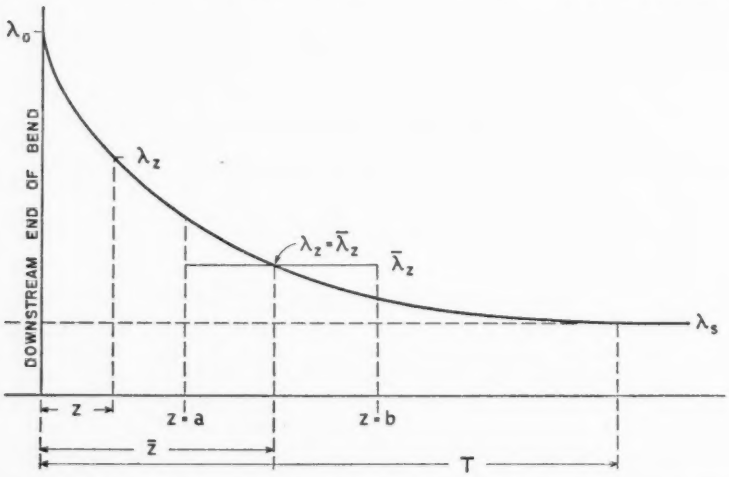


FIGURE 9.—*Diagram showing the resistance coefficient in the downstream tangent as a function of the distance from the downstream end of the bend.*

λ_S at $z=T$, where T does not differ greatly from the distance from the bend to the piezometer connection 7.

3. The slope of the function at $z=T$ should be very small, approaching zero.

These conditions are represented graphically in figure 9.

For the first trial the function was assumed to be

$$(\lambda_z-\lambda_S)=(\lambda_0-\lambda_S)e^{-\alpha z/d}, \tag{10}$$

where λ_0 and α are to be evaluated from the data.

From eq 10 we may write

$$(\bar{\lambda}_z-\lambda_S)=(\lambda_0-\lambda_S)e^{-\alpha \bar{z}/d} \tag{11}$$

where $\bar{\lambda}_z$ is the mean coefficient over the interval from $z=a$ to $z=b$, and $\bar{z}$ is the abscissa of the point on the λ_z curve where $\lambda_z=\bar{\lambda}_z$. These relations are shown in figure 9.

Now if the section $z=a$ to $z=b$ is chosen sufficiently short, as was planned in the layout of the experiments, the value of $\bar{z}$ will not differ

appreciably from the mean abscissa $(b-a)/2$. Hence by plotting $\overline{\lambda}_z$ as a function of $(b-a)/2$, it is possible to determine approximate values for both λ_0 and α. When this was done, it was found impossible to fulfill the conditions set up; that is, the value of λ_z at piezometer 7 was impossibly large. Hence for a second trial the function was assumed to be

$$(\lambda_z-\lambda_S)=(\lambda_0-\lambda_S)e^{-\alpha z/d}\left(1-\beta\frac{z}{d}\right) \tag{12}$$

Now $(\lambda_z-\lambda_S)=0$ when $z=T$, and T is approximately equal to the value of z/d for piezometer 7. Hence to make the right-hand member of eq 12 vanish, we may set $1/\beta=T$ and thus obtain an approximate value of β. Using this value of β, λ_0 and α may be found as before by plotting. The final adopted values for $(\lambda_0-\lambda_S)$, α and β are given

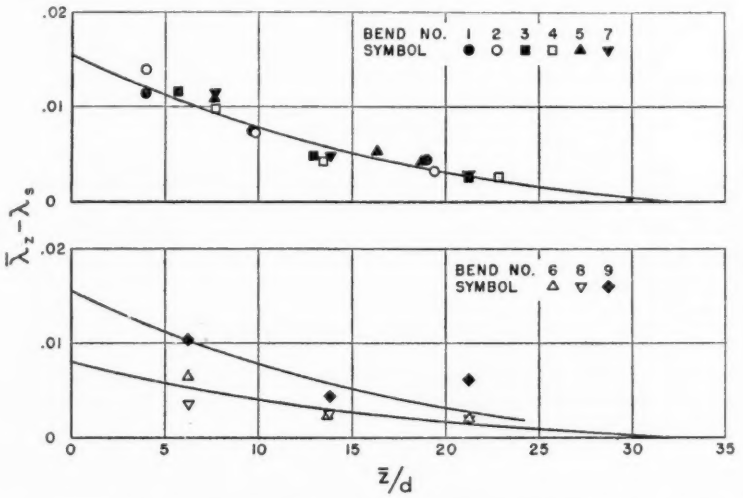


FIGURE 10.—*Experimental results for the resistance coefficient in the downstream tangent as a function of the distance from the downstream end of the bend.*

in table 1. It will be noticed that α equals β in every case. Thus eq 12 becomes

$$(\lambda_z-\lambda_S)=(\lambda_0-\lambda_S)e^{-\alpha z/d}\left(1-\alpha\frac{z}{d}\right), \tag{13}$$

where α has the value 1/32. Finally, from this equation values of $\overline{z}/d$ for each tangent section for each bend were computed by successive approximations.

In figure 10 the experimental values of $(\overline{\lambda}_z-\lambda_S)$ are plotted as functions of $\overline{z}/d$, and the curves represent eq 13 with the values of $(\lambda_0-\lambda_S)$ and α given in table 1. The data for bends 6, 8, and 9 are plotted separately in figure 10 since the results for these bends were erratic and the average values may be considerably in error.

By integration of eq 13 between the limits $z=0$ and $z=T$, we find

$$(\bar{\lambda}_T-\lambda_S)=(\lambda_0-\lambda_S)e^{-\alpha T/d}, \tag{14}$$

where T is the value of z for piezometer 7. Here $\bar{\lambda}_T$ is the mean resistance coefficient for the whole tangent.

But we may write

$$H_T=(\bar{\lambda}_T-\lambda_S)\left(\frac{T}{d}\right)\frac{U^2}{2g}, \tag{15}$$

and this relation combined with

$$H_T=\theta\frac{U^2}{2g} \tag{3}$$

gives for the tangent coefficient

$$\theta=(\bar{\lambda}_T-\lambda_S)\left(\frac{T}{d}\right),$$

and by eq 14,

$$\theta=(\lambda_0-\lambda_S)\frac{T}{d}e^{-\alpha T/d}. \tag{16}$$

The tangent coefficients for each bend, computed by means of eq 16, are given in table 1. Eq 16 was derived only for the purpose of computing the tangent coefficient from the observational data. Unless corroborated by further work it cannot be considered as having any general significance.

4. DEFLECTION COEFFICIENTS

As the pressure indications immediately at the downstream ends of the bends were not reliable, the only way of determining deflection

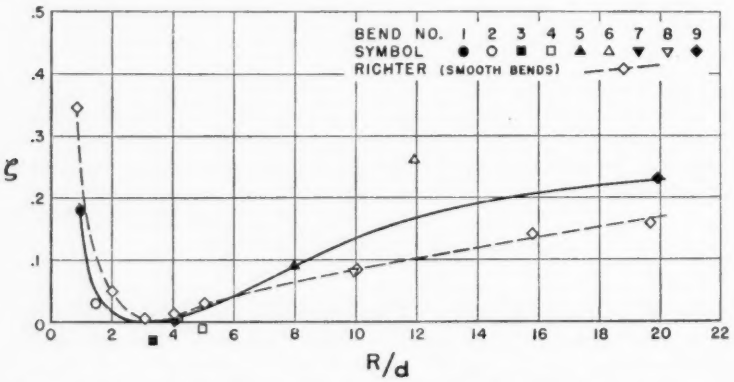


FIGURE 11.—*Deflection coefficients as functions of the relative radius.*

Richter's results for smooth bends are given for comparison.

coefficients was to evaluate the tangent coefficient as in the preceding section and then find ζ from the relation

$$\eta=\zeta+\theta. \tag{7}$$

The results are given in table 1 and in figure 11 where ζ is plotted as a function of the relative radius. Since the tangent coefficients for bends 6, 8, and 9 are possibly subject to large errors, the deflection coefficients for these bends are also open to question. In figure 11, there are also plotted for comparison the values of ζ obtained for smooth pipe by direct measurements by Richter [7].

V. DISCUSSION OF RESULTS

1. RUSTING OF PIPES

The great disadvantage of ferrous pipes for hydraulic experiments is their progressive rusting which results in a continually changing roughness. With care in manipulation, and with unlimited time for the work, it is possible to obtain average resistance coefficients for straight pipes varying not more than about 5 percent from the mean. However, there can be no assurance that the resistance coefficient is the same at all points in the line. The difficulties are increased when dealing with bends, for it is not possible to make determinations of the friction coefficients after a pipe has been bent. The worst effect of rusting, however, appears at the piezometer holes. Here ridges of rust are frequently built up around the holes in such a way as to falsify the pressure indications.

Thus, regardless of the relative magnitude of roughness effects, for a final solution of the bend problem it will be necessary to deal first with smooth pipes and then with pipes of known and unvarying roughness; that is, with pipes artificially roughened. A start in this direction has been made by Hofmann [2].

2. PIPE JOINTS

Very probably some of the discrepancies between results of different observers may be laid to extraneous factors, such as irregular pipe joints, which should properly be excluded in tests of bends. In most of the recent work great care has been taken to set up practically jointless pipe lines as, for example, in Hofmann's and Richter's work and in the work herein reported. However, in some instances the opposite has been the case, the desire being to experiment on pipe lines similar to those in actual practical use. The total effect of irregular joints may become quite appreciable even though the joints appear to be well made. In some unpublished tests of straight 4-inch galvanized pipe with screwed couplings, made at the time of the bend tests, the resistance coefficient was increased 10 percent or more by joints at 10-foot intervals.

3. BEND COEFFICIENT

The results presented in figure 8 show clearly the two flow regimes in 90° pipe bends. For very sharp bends, the bend coefficient drops rapidly to a minimum as the relative radius increases to a value in the neighborhood of $R/d=5$. As the relative radius is still further increased to a value of $R/d=20$, the results of each investigator appear to follow a definite relationship, but no two investigators find the same relationship.

Hofmann's data (fig. 8) apparently establish the fact that roughness is an important factor for bends of relative radius less than $R/d=10$. If this is so, and granting that all the data shown in figure 8 are correct, then it should be possible to establish a relation between the various curves representing the results of the different investigators and the relative roughness of the pipes. For rough pipes we have the relations [8]

$$\frac{U}{u_*}=8.12\left(\frac{r}{2k}\right)^{1/6}, \text{ and}$$

$$\frac{U}{u_*}=\sqrt{\frac{8}{\lambda}},$$

where

u_* = the shear velocity,

k = the absolute roughness, and

r = the radius of the pipe.

Combination of the two relations gives

$$\frac{k}{r}=280\ \lambda^3.$$

From this relation and the published data, values of the relative roughness were computed or estimated. Then the bend coefficients from the curves in figure 8 were plotted against the corresponding relative roughness, as shown in figure 12. For smooth pipe (Hofmann's data) the relative roughness was taken as zero.

While the procedure may not be entirely free from objection, the results in figure 12 are sufficiently suggestive to warrant further work in this direction. It should be stated that Brightmore's data for 3-inch bends have been omitted from figure 12. In these tests he used cast iron bends with galvanized iron pipe tangents. Thus there was no logical procedure for calculating the effective relative roughness.

Conceivably roughness may affect the bend coefficient in three ways. First, the velocity distribution at the entrance to the bend will depend on the roughness of the upstream tangent. Second, the shear at the wall in the bend itself will vary according to the roughness. Third, and probably most important, the excess loss in the downstream tangent will be dependent on roughness. From figure 11 it would appear that roughness has little or no effect on the bend coefficient when the relative radius is less than 6. Hence the greater part of the roughness effect shown in figure 12 must be localized in the downstream tangent. However, further work is necessary before final conclusions can be drawn.

At first sight it does not appear possible to draw any general conclusions from the results in figure 8 for the range of relative radius from $R/d=5$ to $R/d=20$. The following points should be noted, however.

1. The curves representing the data of Davis and of Balch rise from a low value of $R/d=5$ to 7 to a maximum at about $R/d=15$ and then begin to decrease.

2. Hofmann's values indicate the beginning of a much more gradual rise with correspondingly lower values of the bend coefficient.

3. Brightmore's curves start to rise but suddenly drop to low values in the neighborhood of those found by Hofmann.

4. There are two significant irregularities. For a 3-inch bend with $R/d=12$, Brightmore was unable to obtain consistent results. The extreme values are indicated in the figure by the arrows. He states, "in the case of the 3-inch bend with radius equal to 12 diameters, for velocities exceeding 3 feet per second the flow becomes unstable, the loss of head sometimes being much smaller than would be inferred from the losses in the bends of radii equal to 10 and 14 diameters respectively." Also in the present investigation the bend coefficient for bend 8 of relative radius equal to 10 was unexpectedly low. The value obtained is indicated in figure 8 by the isolated point.

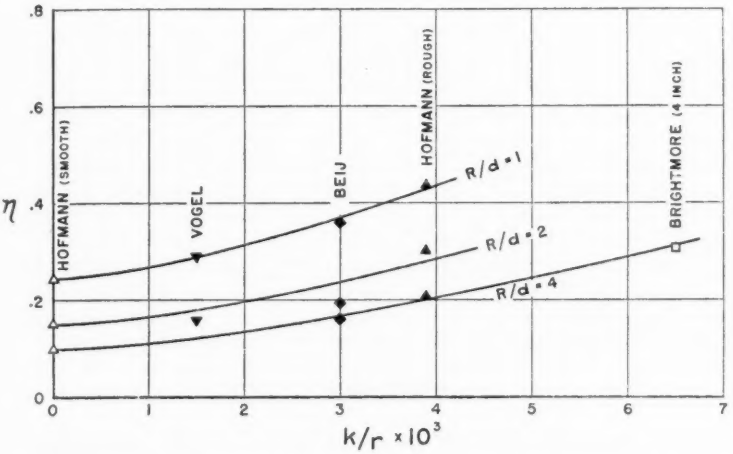


FIGURE 12.—*Bend coefficients for bends of small relative radii determined by various investigators as functions of the relative roughness.*

From the foregoing observations, it may be concluded that in the range from $R/d=5$ to $R/d=15$ or 20 the bend coefficient is not a function of the flow, the relative radius, and the roughness only. Some other variable or variables enter which produce what appears to be a sort of instability manifested by the wide range in results obtained by different or the same observer, and in one case by the very irregular results obtained by one observer for one particular bend. If the explanation is to be found, as seems likely, in relatively small disturbances of entrance conditions, or small geometrical irregularities, then for engineering purposes a curve of maximum values should be established. For this reason the curve in figure 7 was drawn through the highest points.

For bends of relative radii greater than 20 (or perhaps a somewhat larger value) it would seem that the bend coefficient should decrease asymptotically toward zero. While of little importance from the engineering standpoint, this range of relative radii should be explored as the results will very likely be helpful in the solution of the general problem.

4. TANGENT COEFFICIENT

One interesting fact relative to the resistance in the downstream tangent is disclosed by the present investigation. That is, for bends of relative radii less than $R/d=8$, the excess pressure loss in the tangent and the apparent resistance coefficient, λ_0, at the downstream end of the bend are independent of the relative radius. This conclusion is derived from the results plotted on the upper graph of figure 10. This graph shows that the resistance coefficients, and hence the losses, are the same for all six bends of relative radius less than 8. Here again, more precise data covering a wider range of conditions are essential for clearing up the many uncertainties.

5. DEFLECTION COEFFICIENT

The best data on the deflection coefficient appear to be those obtained by Richter [7] for smooth bends. (See fig. 11.) Those obtained indirectly in the present investigation, by comparison, seem to indicate that roughness has little effect in the bend itself, as previously stated.

It will be noticed in figure 11 that the deflection coefficient is zero for a relative radius of about 3 or 4. In other words, the pressure loss in bends of this relative radius is the same as in an equal length of straight pipe. Since the energy loss in the bend must be greater than that in the straight pipe, it must be inferred that the pressure loss does not give the total energy loss. Hence, a complete picture of the bend losses can be obtained only by determining velocity and pressure distributions in successive cross sections of the bends.

VI. FUTURE WORK

For the immediate future at the National Hydraulic Laboratory, work on flow in bends will be limited to smooth pipes and bends. Tests are already under way on coils of relatively low R/d values, and it is hoped that these will be followed by studies of very long bends at large values of R/d.

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MEASUREMENT OF SUPERVOLTAGE X-RAYS WITH THE FREE-AIR IONIZATION CHAMBER

By Lauriston S. Taylor, George Singer, and Arvid L. Charlton

ABSTRACT

A free-air ionization chamber for the measurement of supervoltage X-rays is described. It is built on the guarded-field principle and of such size as to permit measurements for X-ray excitation voltages from 150 to 350 kv at atmospheric pressure and 200 kv upward at elevated pressures. The electrode system is contained in a pressure cylinder of such size as to give an equivalent plate spacing of 4 m at a pressure of 10 atm. The chamber characteristics have been studied in the range of 200 to 400 kv. The most important finding is the required increase in plate separation at the higher voltages. While reasonable, this is at variance with the findings of other workers. From the measurement of the plate separation for full electronic equilibrium, electron ranges may be obtained.

To carry out these measurements it was necessary to design and construct a high-voltage plant capable of extreme steadiness of operation. This was accomplished with a four-stage rectifier having valves operated on a single pumping system. Potentials were carefully distributed through the system with the result that the voltage could be measured and controlled within $\pm\frac{1}{4}$ percent, which figure also represents the variation in tube output.

The X-ray tube is of the simple four-stage type, made up of Pyrex-glass cylinders. By means of an insulated target, only the target current is measured.

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I. INTRODUCTION

The internationally accepted definition of the unit of X-ray quantity has from the first been based upon the ionization produced in a unit volume of unrestricted air [1].[1] The original definition was, in fact, a statement of the physical requirements for reproducing a unit in terms of the ionization in a free-air ionization chamber. This unit has served its purpose very well for the X-ray voltages in use up to within the past 3 or 4 years. However, with excitations in excess of 200 kv, various mechanical and physical difficulties have appeared to limit the applicability of the definition, as well as of the free-air ionization chamber used to determine it.

Consequently, there has been an increasing trend toward the use of thimble chambers for the fundamental realization of the roentgen. The theoretical as well as experimental evidence favoring this trend appears to be reasonably sound, particularly as regards theory. Experimentally the problem has presented great difficulties which, in the hands of a few experimenters, seem to have been adequately overcome. There remains, even for them, the problem of definitely and irrefutably tying together the thimble-chamber measurements in the supervoltage region with free-air measurements in the high-voltage region. The thimble-chamber measurements appear to be self-consistent, but it is definitely desirable to check them by a wholly independent means and at the same time correlate them with the free-air measurements at the lower voltages.

In order to validate thimble-chamber measurements in the supervoltage region it has been necessary to redefine the roentgen. This was done at the Fifth International Congress of Radiology [2] as follows: "The roentgen shall be the quantity of X or gamma radiation such that the associated corpuscular emission per 0.001293 gram of air produces, in air, ions carrying 1 e. s. u. of quantity of electricity of either sign." It is not proposed to discuss this definition in its relation to thimble chambers; it has already been ably done by Mayneord [3, 4], Lauritsen [5, 6, 7], Gray [8, 9, 10], Laurence [11], Failla [14], and others. In connection with the use of free-air chambers,[2] however, two points of prime importance must be mentioned. First, the physical magnitude of the unit is exactly the same as in the older definition for excitations below about 200 kv (peak). Second, the new definition removes the question of inclusion or exclusion of scattered radiation in free-air measurements made in the supervoltage region—a question which had been troubling the American X-ray standardization committees for some years [12]. The new definition therefore makes it possible and desirable to extend the useful range of the free-air chamber up to indefinitely high voltages, provided the design characteristics can be adequately worked out in conformity with the definition. It is the purpose of this paper to describe equipment designed for the investigation of these problems and to report measurements obtained in the 200- to 400-kv range, designed to test the conditions essential for realizing the definition of the roentgen. It should, of course, be emphasized that the particular design employed in this study is not necessary in all cases,

[1] Numbers in brackets refer to the citations listed at the end of this paper.
[2] "Free-air" ionization chambers may be classed roughly as those in which chamber walls contribute nothing to the measurement. This may, of course, include chambers operated above atmospheric pressure.

but was so chosen as to yield the design factors for any particular voltage range desired.

We will review very briefly the several investigations of free-air ionization chambers for the measurement of supervoltage or gamma radiations, and point out what appears to us to be the limitations of each of these several studies insofar as relates to X-ray measurements.

The first free-air chamber for extra-hard radiations was constructed by Failla [13] in 1931. This had a maximum plate separation of about 1 m and a length of about 1.5 m. Field correction was provided by means of the guard-wire principle such as developed for our lower-voltage chambers [15]. Because of size limitations this chamber did not prove successful in the measurement of gamma rays. Failla was also unable to use it with X-ray voltages above 200 kv since the available treatment room was too small.

Mayneord [16] and his coworkers (1934) constructed a parallel-plate ionization chamber having a maximum plate separation of 20 cm and plate length of 50 cm. For this a field correction was found unnecessary. Their results indicated that a plate separation of 20 cm was sufficient for X-ray potentials up to 400 kv, and apparently also for gamma rays. However, as the measurements with this chamber showed marked divergences from the thimble-chamber measurements above 250 kv they discarded the parallel-plate chamber as a primary standard. They gave insufficient distance between limiting diaphragm and collector as one of the main design limitations affecting the attainment of radiation equilibrium in the ionized volume.

Lauritsen [5] used a parallel-plate chamber for voltages up to 900 kv. With a plate separation of 30 cm, radiation equilibrium was apparently obtained by placing the chamber at a considerable distance from the limiting diaphragm and using a very narrow beam of radiation. No direct evidence for the adequacy of the 30-cm plate spacing was given. In a personal communication he showed a Wilson cloud-expansion photograph of a narrow 700-kv X-ray beam wherein the tracks appeared to be limited to a region about 10 cm on both sides of the beam. No data were given tying directly his supervoltage measurements to high- or low-voltage measurements.

Jaeger [17] has reported on the use of the PTR Fasskammer at voltages up to 500 kv, and shows perfect agreement with his "Universalkammer" for X-ray voltages from 10 to 500 kv. His free-air chamber is 25 cm in diameter, with the collecting electrode parallel to and about 4 cm from the axis and the collimated X-ray beam. Using lining sleeves of different diameters placed in this chamber, he apparently proves its size to be adequate. This conclusion is very difficult to reconcile with our finding that a 12-cm plate spacing is just barely sufficient for the measurement of 180-kv X-rays.

Kaye and Binks [18, 19] have described a large free-air ionization chamber also employing the guarded-field principle and having a plate spacing of some 3 m, which they used for measuring gamma rays. They have not reported any measurements with X-rays.

Of these various studies, Mayneord's [16] and Jaeger's [17] appear to be the most complete and yet their essential results are contradictory. We have endeavored therefore to set up an experimental arrangement which permits the overlapping of the conditions of their investigations.

II. HIGH-VOLTAGE EQUIPMENT AND X-RAY TUBE

1. GENERAL REQUIREMENTS

For the investigation outlined above, as well as to provide suitable equipment for future standardization work, it seemed advisable to construct a special tube and voltage-rectifying system containing certain features conducive to the elimination of some of the uncertainties present in earlier work.

The principle requirements were: (1) A small and steady focal spot, (2) a very steady tube voltage and current, (3) a reasonably small ripplage, (4) a minimum of filtration between the target face and ionization chamber, and (5) as large a distance between target and chamber as might be necessary.

2. RECTIFIER CIRCUIT

The electric circuit shown in figure 1 is a simple cascade of four half-wave rectifiers designed to give 150 kv (constant) each. Successive units above the first were supplied through 1:1 insulation transformers

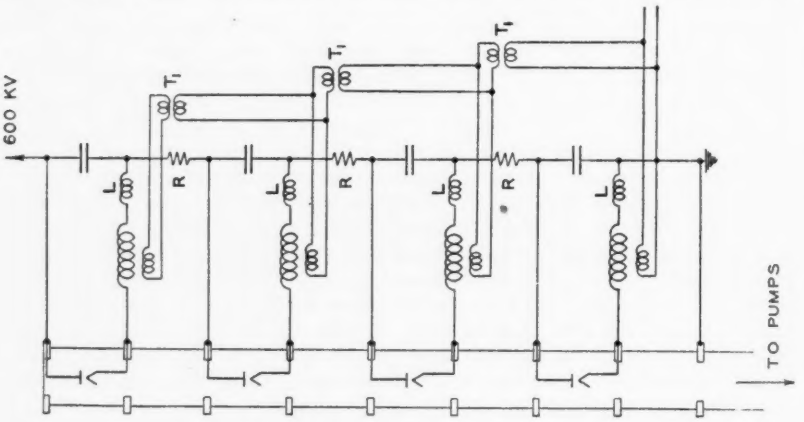

FIGURE 1.—*Schematic diagram of 600-kv d-c. rectifier system.*

(T_1), of the toroidal type having only oil insulation. Each unit was connected to its neighbor through 0.5-megohm (Glo-bar) noninductive resistors (R). The main transformers were isolated from the remainder of the circuit by small radio-frequency chokes (L), each made up of 2 lb of size 6 AWG copper wire wound on a 2-in. Bakelite tube.

Each 150-kv unit was placed on a wood frame supported on porcelain insulators.

Galvanized-iron "down spouting" was used for most of the conductors above 150 kv. Otherwise, little precaution was made for the avoidance of corona. Mutual shielding of many of the components apparently helped because at 400 kv, corona was neither excessive nor troublesome.

The filaments of the four rectifiers were supplied by four 1:1, 15-v insulation transformers (*T2*) connected in series and resting atop the main transformers (*T3*) as shown in figure 2. The rectifier tubes were made for continuous evacuation by a single apiezon oil-diffusion

FIGURE 2.—*Rectifier system and X-ray tube, looking down from one corner of the room.*

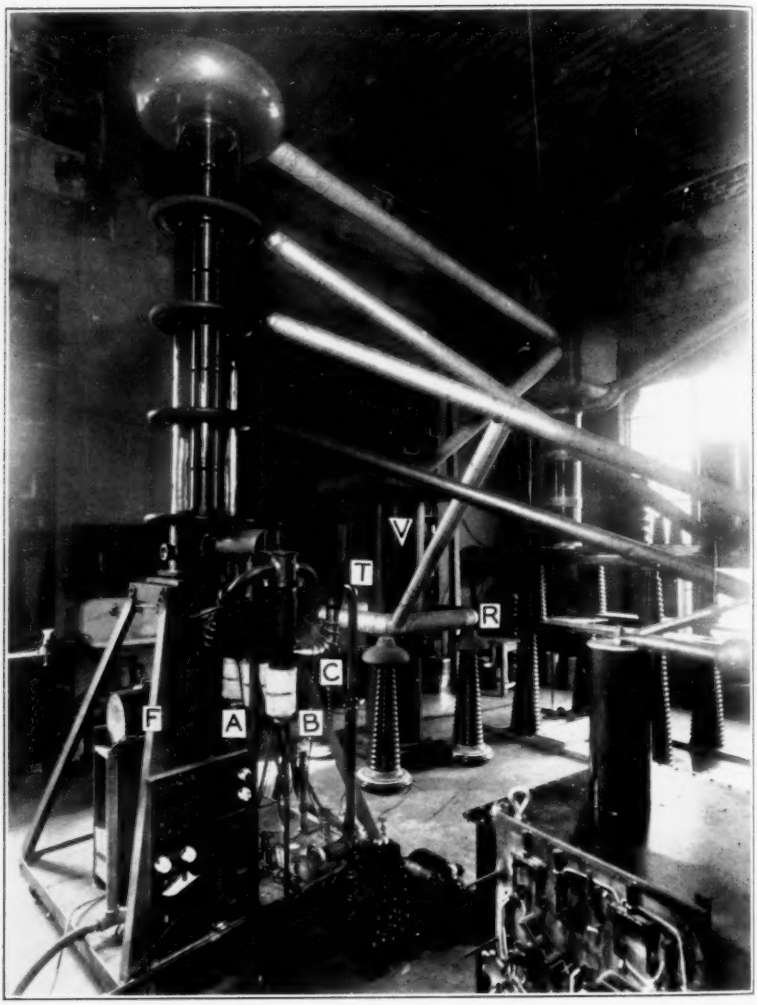

FIGURE 4.—*X-ray tube and voltmeter* (*V*).

pump system [20]. Tubes of 8-in. Pyrex glass 40 in. long served as the envelope for each rectifier, which was designed for a maximum inverse voltage of 300 kv. Each electrode consisted of a 4-in. brass tube ending with a ½-in. diameter reentrant steel beading. The filaments (*F*, fig. 3) made up of 134 mm of 15-mil tungsten, were each

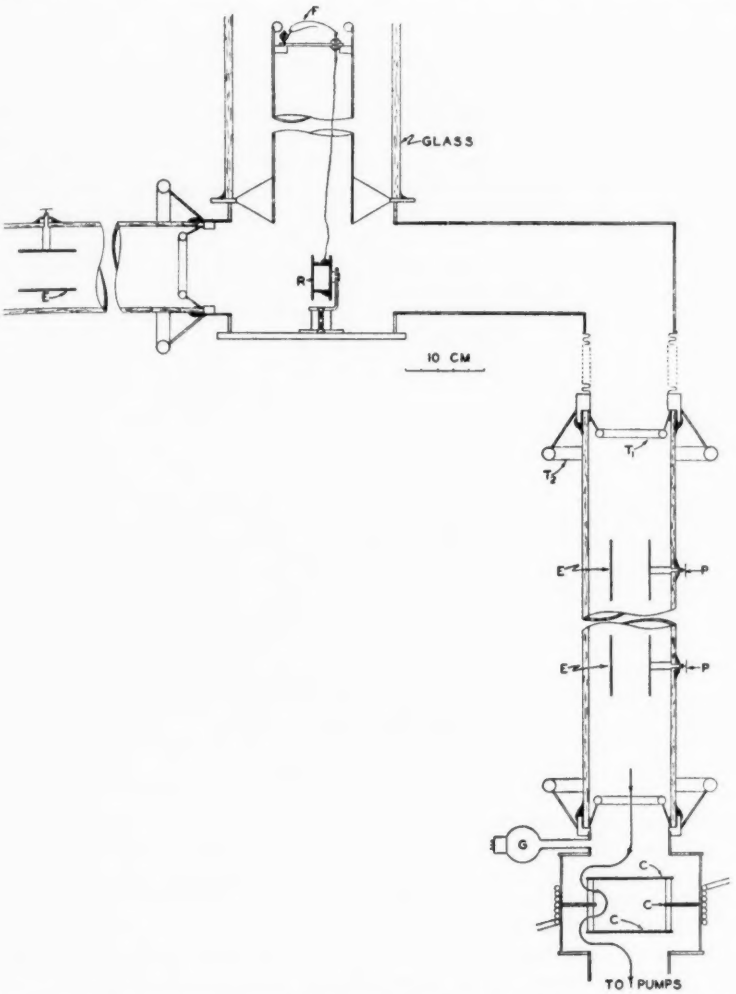

FIGURE 3.—*Cross sections through the pump baffles and the manifold of the first rectifier tube*

bent in two open loops toward the anode but not extending beyond the plane of the end of the cathode. Operating characteristics showed a space current of about 20 ma at 1,000 v, for a filament current of 10.7 amp. The filaments could be readily removed for replacement, by removing a waxed-on cover and reaching through the anode from the top of the tube. One filament lead was fastened to the electrode and the other to a self-winding reel (*R*) at the bottom of the manifold.

3. PUMPING SYSTEM

The pumping system consisted of two 4-in. "fine" apiezon oil pumps feeding into a third "coarse" pump and all backed up by a Cenco Hypervac-20 pump. Baffles between the fine pumps and the glass system consisted of alternate copper rings (C) and disks, all soldered together and water cooled (fig. 3). Although the glass above these baffles shows a pronounced yellowing, the occasional gas discharges in the tube show a definite absence of oil vapor. When first assembled no electrodes of any sort were placed in the 4-in. tubes connecting the rectifiers. With this arrangement the long mean free path was conducive to electrical breakdown and limited the over-all voltage to about 200 kv, at which point gas discharge occurred throughout the connecting tubes; but this discharge condition has apparently been completely eliminated by placing in each tube, two brass electrodes (E) of thin tubing 2 in. in diameter and 3 in. long (figs. 2 and 3). These electrodes were connected, through holes drilled in the glass tubing, to small outside points (P) which, through field pick-up, allowed the rings to assume their proper potential. Toroids (T_1 and T_2) inside and outside the connecting tubes at the ends protected the seals from puncture, respectively, in case of a heavy discharge. The only puncture experienced was opposite the filament of one rectifier where there was a large air-bubble flaw in the glass envelope.

A pirani gage in the forepump line served as an indicator for the pumping speed. An ionization gage (G) located immediately above the cold baffle on one pump gave a continuous indication of the working vacuum. A second ionization gage at the base of the last rectifier proved very useful in hunting leaks. All the gage meters and controls (as well as a similar set on the X-ray tube) were located on a single panel (A) in the control room, (fig. 10), and were invaluable for studying the operation characteristics of the equipment. The working vacuum was about 3×10^{-6} mm of mercury, and with the system shut off the pumps for 6 weeks the vacuum remained at a value of 10^{-3} mm or better (the limit of reading the pirani gage).

4. X-RAY TUBE

It was not desired to do any unnecessary development work in the construction of our X-ray tube, so we have followed as closely as possible the design used so successfully at a million volts for nuclear physics investigations at the Department of Terrestrial Magnetism, Carnegie Institution [21].

The tube is designed for 600 kv and consists of four sections of Pyrex-glass cylinders 12 in. in diameter by 18 in. long (fig. 4). The electrodes were 5 in. in diameter with reentrant rolled-steel ends. Adjacent accelerating tubes were separated by a ½-in. gap. Following Tuve [21], these electrodes were very accurately aligned during assembly by means of a long mandrel. The glass cylinders and electrodes were assembled on the floor and held in place with tie rods while the wax (Pizein) joints were made. The resulting unit was then lifted into place atop the pump manifold, the tie rods being kept taut until after the tube was evacuated. They were always replaced before letting air into the system. While this procedure caused a little more

trouble than with direct assembly (as first tried), it eliminated troublesome cracking of the seals from unavoidable strains.

The pumping system for the X-ray tube is somewhat faster than that used, for the rectifiers, since it was possible here to eliminate some of the long delivery tubes. The arrangement of the two fine pumps (A) and one coarse pump (B) is shown in figure 4. The use of toilet bends (C), sink traps (T), etc., eliminated many soldered joints, as is evident from the figure. All pump connections were made with the rubber gasket seals described by Rose [39]. The pressure gages duplicated those of the rectifier system and were read at the same panels.

All operating components of both tube and rectifier were protected by an electrical interlock system to prevent errors in operation. This insured the following starting order: (1) Forepump, (2) water supply, (3) pump heaters, and (4) transformer voltage. A failure of any one would cut off all higher components and necessitate manual resetting.

(a) FILAMENT

The filament construction is essentially of the cup focusing type shown in figure 5. Provision is made for complete adjustment while the tube is in operation. The main filament housing (A) is made of thin steel tubing, 2½ in. in diameter, extending down nearly to the center of the first glass section. Facing the filament cup is the first accelerating electrode (B), a flared steel tube of about the same diameter. The filament is supported on a Lavite bushing (L), which may be centered by means of the setscrews (C). Filament leads are insulated from the main housing to permit the use of biasing potentials if necessary. Vertical adjustment of the filament assembly of about 1 cm is effected with an external pulley (P), the displacement being provided for by a Sylphon bellows (S_1). A lateral adjustment up to 1 cm from the center in any direction is effected with a double ball-bearing eccentric, as described by Tuve [22], the seal being secured with the Sylphon bellows (S_2).

The total distance from filament to target is about 8 ft. and within this path appreciable deflection of the cathode beam may be produced by the earth's magnetic field. This becomes very troublesome at the lower voltages. It was eliminated by lining the accelerating tubes with a double layer of 0.014-in. heat-treated Chrome Permalloy.

(b) TARGET

The target construction is shown in figure 6. The most essential feature is its complete insulation by means of a glass gasket (G) to permit the use of a milliammeter in the ground circuit. The target (T) is of lead, electroplated on copper and mounted at the bottom of a brass tube ⅛-in. thick and 5-in. in diameter in the manner described by Folsom [23]. At the point of emergence (W_1) of the X-ray beam, this tube was milled down to a uniform thickness of about $\frac{1}{32}$ in. Surrounding the entire target tube is a 6-in. water jacket. This is provided with a reentrant window (W_2) (opposite the target window W_1) covered with $\frac{1}{64}$-in. brass and extending in so as to nearly touch W_1. Thus the total inherent filtration of the tube consists of $\frac{3}{64}$ inch of brass plus about 2 mm of water.

Extending down into the target tube, and spaced ⅛ in. from it, is a thin steel tube (L), which is insulated from both ground and the

target. This shield tube is connected with the control room and serves three purposes: (1) It prevents the bulk of the scattered electrons from striking the target tube, so that the milliammeter (M_1) gives very nearly the true target current; (2) it permits the

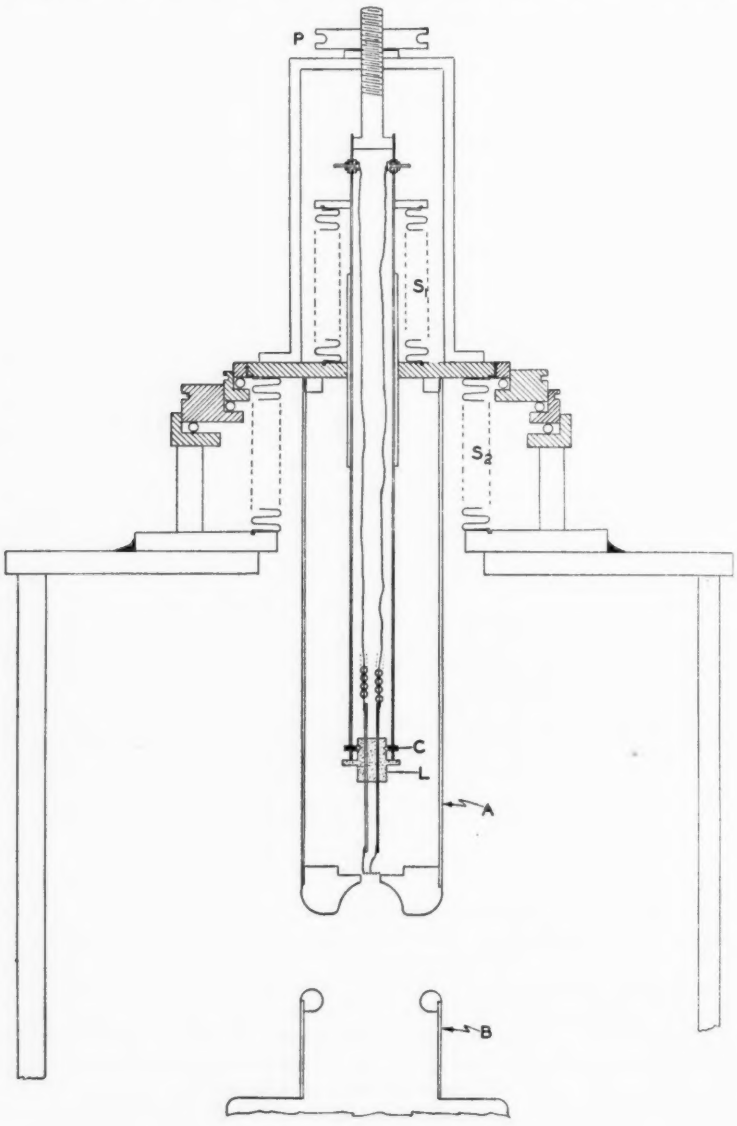

FIGURE 5.—*Filament assembly.*

remote reading of the current to the shield and thus allows adjustment of the focusing conditions to obtain the optimum ratio of M_1 to M_2; and (3) it operates through a sensitive relay (R) to open the circuit-breakers in the transformer circuit in case of a general gassy

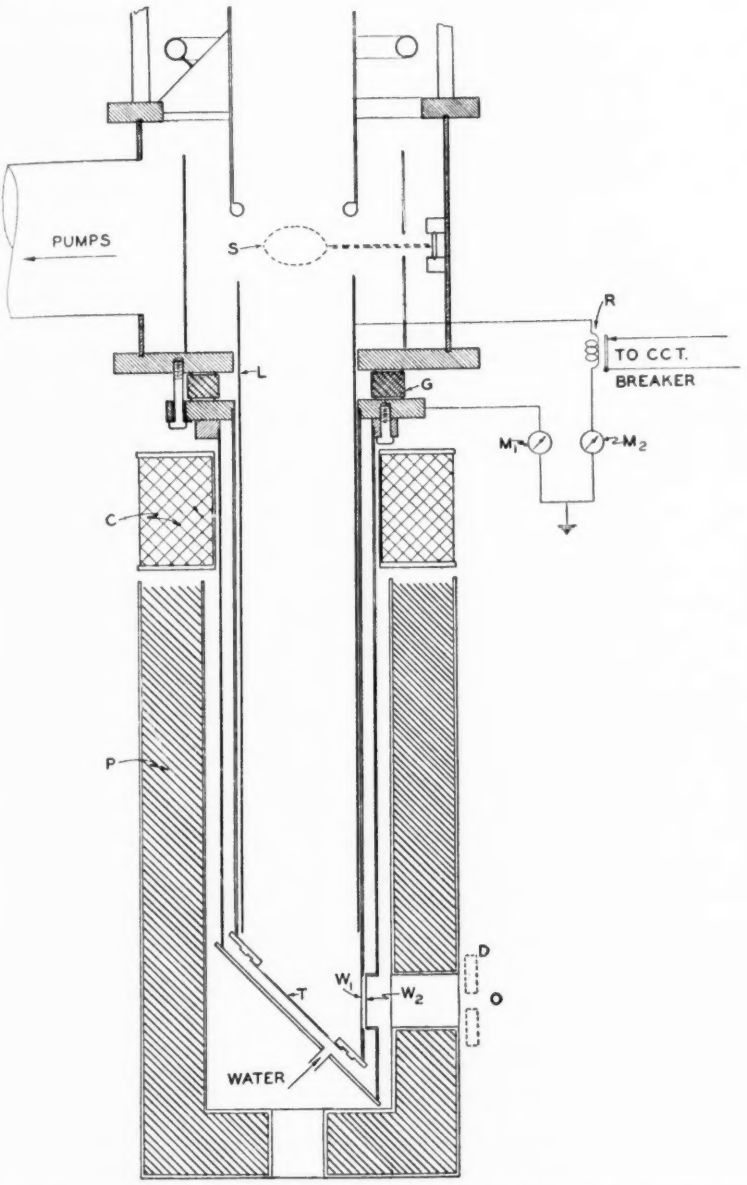

FIGURE 6.—*Cross section through the earthed end of the X-ray tube, showing target details, focusing coil, etc.*

condition of the tube. This last result is brought about by the fact that the presence of a general "gassy" condition throughout the tube defocuses the electron beam, causing it to strike the shield and pass a releasing current through the relay circuit. This action was found

to be very positive and quick, making it virtually impossible to overload the tube and destroy the target.

The target was surrounded by a double-walled iron jacket filled with 1.15-mm lead shot (*P*) to a thickness of 2½ in. in all directions, except for the two 2-in. openings shown. This effectively restricted the radiation to a narrow beam and also greatly simplified the protection problem in the X-ray tube room. An electromagnetically operated lead shutter was placed adjacent to the horizontal opening (*O*).

(c) FOCUSING

It was desired to have a reasonably small and uniform focal spot which is effectively a point source for a distance of 2 m or more. Direct focusing from the filament cup gave a focal spot 5 to 7 cm in diameter with a greater concentration of the electrons near the periphery. To reduce and control the size of the focal spot a focusing coil (*C*) was used [24]. This consisted of 4,500 turns of size 18 AWG copper wire wound on an insulated spool 2¾ in. deep and 3¾ in. along the axis. A focal spot of 2 cm or less was readily obtainable with a current of about 0.7 amp through the coil, the size remaining nearly constant over the voltage range of 200 to 400 kv. The current through the focusing coil was held constant by means of an ordinary hydrogen-filled ballast lamp.

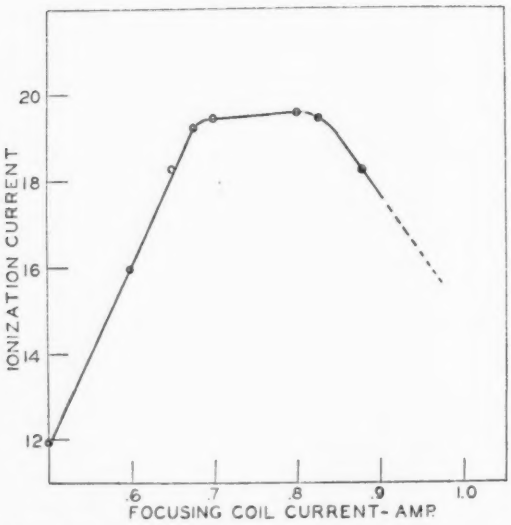

FIGURE 7.—*Effect of focusing coil current on the radiation leaving the tube through a small diaphragm.*

Central alignment of the beam was determined by means of a fused-quartz screen (*S*) that could be swung in and out of the beam through a rotary Sylphon joint and observed through a glass side window while the tube was in operation. Any necessary focusing adjustment was obtained with the double eccentric-filament adjustment described above and operated by strings from without the X-ray tube room.

The size of the focal spot was determined within the desired limits by limiting the beam with a 3-cm diaphragm (*D*) located near the target, and then measuring the X-ray output with an ionization chamber some 3 m away. Figure 7 gives a typical curve of the ionization current as a function of the current in the focusing coil. The flat peak shows that the focal spot did not overlap the temporary diaphragm and hence was of somewhat less diameter. Numerous pin-hole photographs verified these conditions and also showed a negligible amount of off-focus radiation. For normal operation a focusing-coil current at the peak of the curve was employed.

(d) DISTRIBUTION OF CURRENT IN THE X-RAY TUBE

Simultaneous measurements of the target current, shield current, and current input to the high side of the tube gave a further check on the completeness of the focusing. In all cases the sum of the target and shield currents equalled the total input current within the limits of accuracy of the meter readings. Also the target current bore a very nearly constant ratio of about 4:1 to the shield current for all voltages and tube currents used. To test for secondary radiation arising from scattered electrons striking the ends of the accelerating tubes, a pin-hole X-ray exposure of the entire tube was made; but an hour's exposure failed to reveal any image on the film.

5. VOLTAGE CONTROL AND MEASUREMENT

Input voltage for the main transformers is supplied by a 25-kva 60-cycle generator driven by a 40-hp synchronous motor. The generator voltage was applied directly to the transformers with essentially no resistance in the line. Voltage was regulated through field rheostats located in the control room, and adjustable in steps as small as .02 ohm out of a total of about 50 ohms.

Output voltage was measured directly at the X-ray tube terminal with a 600-kv resistance voltmeter (V), as described by Tuve [25] (fig. 4). The resistance elements and corona shields are contained in a vertical Bakelite tube sealed to prevent the entrance of moisture. To assist in obtaining a uniform potential gradient along the Bakelite tube, a potential ring (R) is placed about its center and connected to the midpoint of the voltage cascade.

The resistance was calibrated under full working conditions against our standard 200-kv shielded resistance voltmeter [26], which has an over-all accuracy of $\pm \frac{1}{4}$ percent or better. To do this, the 600-kv resistor was tapped off at intervals corresponding to 200 kv, and compared directly with the standard up to that voltage. Repeated checks have shown the resistor to be reliable within the desired limits of accuracy ($\pm \frac{1}{8}$ percent).

6. TUBE CURRENT CONTROL

The X-ray tube filament is heated with storage batteries located in a corona shield atop the last voltage cascade. A coarse hand-operated rheostat gives a preliminary current setting. Fine control is effected by two remotely operated motor-driven rheostats of which one gives a continuous adjustment over a range of about 0.1 ohm, and the other an adjustment over a range of 0.8 ohm in 25 steps. Readings of the tube current were made with a milliammeter (M_1) (fig. 6). For control purposes a galvanometer with a displaced zero is used which renders the current easily controllable within 1 ma in about 1,000 ma.

Occasional variations of 1 or 2 percent in output were noted in spite of apparently steady tube current and voltage. These changes usually took place after a slight gassing or other disturbance and were no doubt caused by a slight change in the focal spot.

To eliminate this a multiplate-control ionization chamber (F, fig. 4) was placed in the beam immediately next to the shutter. The tube current was adjusted to hold the control ionization current steady

at a given value of the tube voltage. By this means it is possible to hold the radiation output constant within $\pm\frac{1}{4}$ percent over the period of a whole day. It is observed that, using this method of control, the target current does not depart from its steady value by more than 1 or 2 percent.

III. STANDARD FREE-AIR IONIZATION CHAMBER

After reviewing the investigations outlined in the introduction, it was felt that no one of them offered the best solution to the problem of establishing a free-air standard X-ray ionization chamber. One of the principal difficulties was judged to be the inadequacy of the methods of comparison with accepted standards in other voltage ranges.

1. PRESSURE CHAMBER

It was decided to construct a chamber to operate under a moderate air pressure, thereby reducing operating dimensions to practicable magnitudes. The need was a single ionization chamber capable of measuring X-rays in roentgens, under the following conditions: (1) At elevated pressures X-rays from 200 kv upward; (2) at atmospheric pressure X-rays from 300 kv downward; and (3) at such plate separations that field correction is unnecessary. It was also necessary to be able to determine air absorption corrections under all operating conditions.

The completed ionization chamber consists of a steel pressure cylinder 30 in. in diameter and 7 ft long (inside). The rear end is completely removable (figs. 8 and 9). Air is pumped in through a calcium chloride drier, and in addition several trays of drier are kept in the cylinder. Temperature within the chamber is measured with a thermometer fastened to the electrode assembly and read through a thick glass window at the rear.

The pressure is read and controlled from a multiple mercury manometer (*B*), as described by Meyers and Jessup [27], located in the control room (fig. 10). The manometer tubes are of carefully selected Pyrex glass; and successive mercury columns are hydrostatically coupled with thoroughly outgassed distilled water. Each mercury column height is determined by means of a hairline ruled on a glass slider moving on a meter bar. Mirrors behind the columns prevent parallax. Settings can be read within ± 0.1 mm, making a possible over-all error on all eight columns of ± 0.8 mm, or about 1.5 mm maximum. At 1 atm this amounts to a maximum error of very close to 0.1 percent, which is closer than warranted by other experimental inaccuracies present.

The negative pressure effect of the water column is automatically obtained with each mercury column reading, excepting the two end columns. The end columns terminate in the center of heavy glass bulbs contained in brass protective shields (*C*) and having a cross-sectional area about 250 times that of the manometer tubing. Consequently for a maximum motion of one water column of 50 cm the change of the end water level will be only 0.2 mm, giving a difference between the levels in the two bulbs of 0.4 mm of water or 0.03 mm in mercury, which can be entirely neglected. Temperature-density corrections for the water and mercury are small for ordinary temperature changes and may usually be neglected.

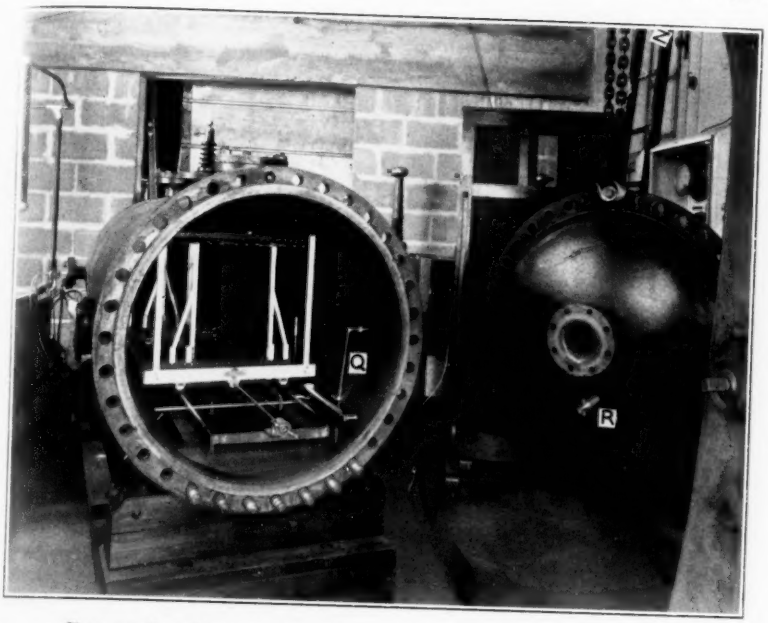

FIGURE 8.—*Pressure ionization chamber with rear end removed.*

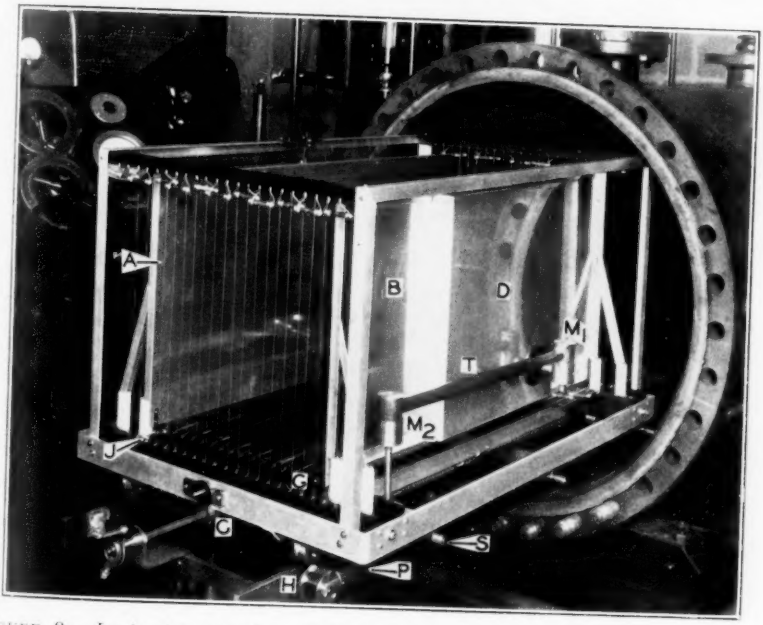

FIGURE 9.—*Ionization chamber electrode system drawn out of rear of pressure chamber.*

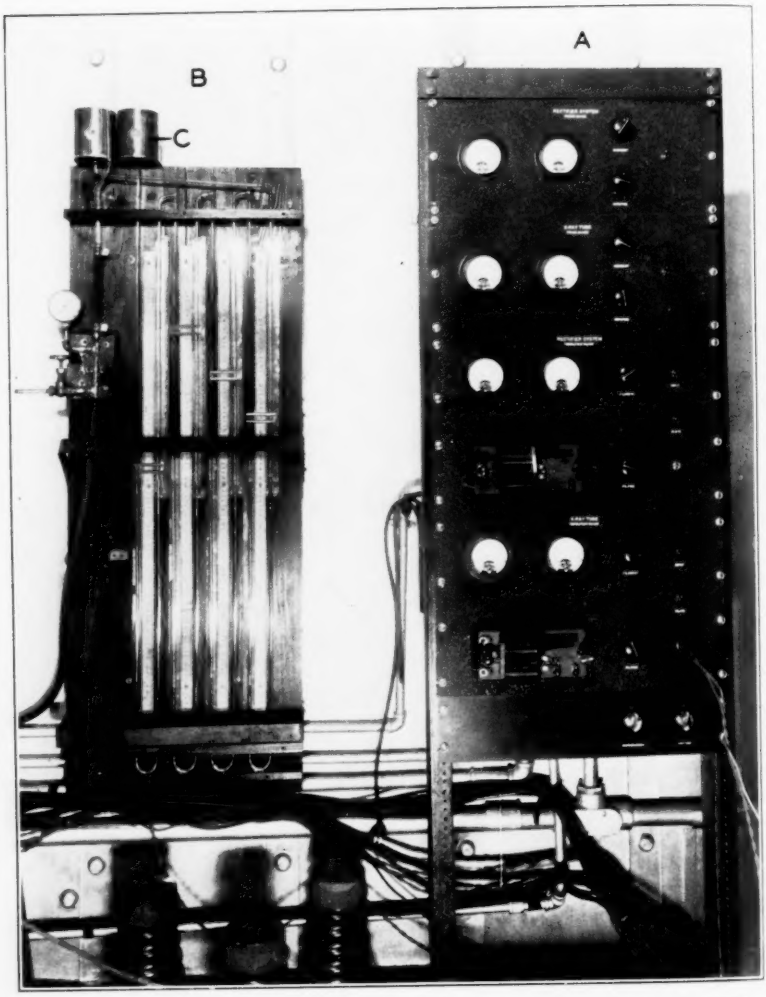

FIGURE 10.—*Details of the multiple tube manometer and vacuum gage panel.*

For the calibration of the meter bar and for control purposes a vertical cathetometer is employed. This is easy on the eyes and permits a pressure control within 0.05 mm of mercury on a single column.

2. ELECTRODE SYSTEM

The electrode system is shown in figure 9 in which the entire assembly is pulled partially out of the rear of the chamber. The high-potential plate (*A*) and collector plate (plus guards) (*B*) are mounted on cross slides. By means of a pinion and rack (not visible) driven by the gear train (*C*) the two sets of plates may be moved smoothly toward or away from each other. The motion is transmitted to the lower gear through a sliding collar on a square shaft extending the length of the track and this in turn through a rotary Sylphon seal (*R*) in the rear of the chamber.

The over-all length of the plates is about 750 mm; the effective length of the collector (including air gap) is 254.0 mm, and each guard plate is about 25 cm wide. The minimum plate separation is 7.2 cm, and the maximum, 38 cm. The height of the collector being about 35 cm, a plate separation greater than 35 cm is never ordinarily used since this would cause a loss of some of the ions under conditions where full plate separation is necessary to their full utilization.

In accordance with previous analyses [28, 29], a guard plate width of 25 cm will permit the use of a plate separation of only 16 to 18 cm without introducing field distortion at the edges of the collector. For greater separations therefore it is necessary to resort to the method of guarding developed in this laboratory [30, 31] for low-voltage ionization chambers.

3. FIELD CORRECTION

In this case aluminum guard wires 0.4 mm in diameter and 2 cm apart were extended completely around the ionization volume of the chamber except for the small gap (*G*) near the lower corners to permit the displacement of the plates. The potential of these guard wires was uniformly distributed by insertion of a series of 2-megohm metallized resistors some of which may be seen across the top Bakelite spreader.

To insure full field correction it is important that the potential of the guard wires be uniformly graded between that of the high-potential plate and the grounded guard plate. Therefore, for small plate separations, only those guard wires falling between the plates are charged. For this purpose the high potential is applied directly to the collector plate and from there to the guard wires by means of the sliding contact (*J*). Similarly, the ground is applied directly to the guard plates and to the other end of the guard wires by means of a like contact. These two sliding contacts also serve to tie in the set of guard wires extending along the bottom of the chamber, which otherwise would be isolated.

Since it was planned to use saturation potentials as high as 10,000 v on the chamber, the possibility of corona from the guard wires had to be tested. At 15,000 v a spark-over occurred at some point within the chamber but below this voltage no effect of corona was detectable with the current-measuring system.

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The entire electrode assembly is mounted on a welded steel track running the full length of the cylinder. The displacement along the track is effected through a sprocket and gear drive operated from without the tank through a pressure-tight rotary Sylphon joint.

4. STRAY IONIZATION

To avoid picking up any stray ions or electrostatic disturbances the entire conductor system leading from the collector plate to the electrometer was shielded. The collector itself is shielded by an aluminum cover (D). From there the conductor passes through two swivel joints (M_1 and M_2) and a section of telescoping tubing (T). From M_2 the lead passes down to a brushing contact on an insulated rod located centrally in tube P (1½ in.) extending the length of the track. A ½-in. sector of this tube is cut out at the top to permit insertion of the brushing contact. To close this long opening electrostatically, a strip of thin spring steel (N, fig. 8) is stretched along the top and bottom passing over the rollers (H) at the ends, and moves with the chamber so as to always keep the slot covered. A gooseneck connection (Q) leads from the bushing (S) through a pressure-tight seal to the outside of the chamber. The entire electrical system is insulated with highly polished amber and no leakage difficulties have been experienced.

Careful tests were made to detect any stray ionization in this conductor system. The currents being normally measured by a null method, there should be no potential difference between the electrometer leads and the earthed shields. At normal working current sensitivities (10^{-13} to 10^{-14} amp/mm deflection) no evidence of stray ionization currents was found even with an 8-in. entrant beam of X-rays. When a deflection method of measurement is used, the conductor may be at a potential several millivolts different from ground, but even under these conditions no stray ionization has been detected.

However, at the highest sensitivities (5×10^{-15} amp/mm) various difficulties were encountered. Ionization from cosmic rays and alpha-particle contamination produced a slightly unsteady background current amounting to 3 or 4 percent of the total measured current at atmospheric pressure. This was, of course, unavoidable.

Of greater concern was the effect of contact potentials within the insulated system at the very high sensitivities. These gave rise to very uncertain and unsteady stray ionization currents which varied with the plate separation, size of the X-ray beam, etc. These spurious effects were eventually reduced to a workable minimum even at our highest sensitivity. The greatest single source of stray ionization was between the guards and collector electrode where the spacing is only about 0.5 mm. This was largely eliminated by making the three plates out of a single sheet of aluminum, taking care that they were kept in the same relative position as before cutting. In addition, the inside of the tank was scraped and then painted with "Graphite Acid Seal" paint, which we had found by separate tests to establish little contact emf with respect to aluminum or itself.

When using a broad beam at voltages above 360 kv, some radiation entered the front of the chamber through the several inches of steel making up the various flanges and supports. This was avoided by

placing a lead baffle 3 ft square and ½ in. thick, on a frame in front of the chamber, with a 3-in. opening to permit passage of the X-ray beam. The 2½-in. window at the fore end of the chamber was sealed with 0.5-mm aluminum, which will withstand pressures up to at least 4 atm. In front of this is an electrically operated shutter and a rack for holding a large number of lead and copper filters, which could be shifted in and out of the X-ray beam from within the control room.

The entire assembled chamber was supported on a rigid frame, which, in turn, was mounted on a 20-ft track running parallel to the useful X-ray beam. Thus target-diaphragm distances ranging from 2 to 6 m were obtainable.

5. DIAPHRAGMS

Since the cross-sectional area of the limiting diaphragm appreciably affects the accuracy of measurement, it is essential that it be known with an accuracy of ±0.1 percent. As pointed out in connection with previous high-voltage X-ray measurements, this is difficult of attainment and was finally reached through the use of hard-gold diaphragms made by plug gage methods [31,32]. More recently it has been found possible to make hard-lead diaphragms by similar methods, relying for their final accuracy upon comparisons with the gold diaphragms. International agreement [33] requires that limiting diaphragms be cylindrical and of such thickness that not more than 0.1 percent of the intensity of the useful transmitted beam passes through the walls of the diaphragm. The use of thick diaphragms necessitates great care in alignment in the beam, since poor alignment reduces the effective area of the opening. Furthermore, at short diaphragm-target distances, a thick diaphragm introduces some uncertainty as to the proper position for placing a thimble chamber under calibration, or as to the application of any inverse-square law corrections.

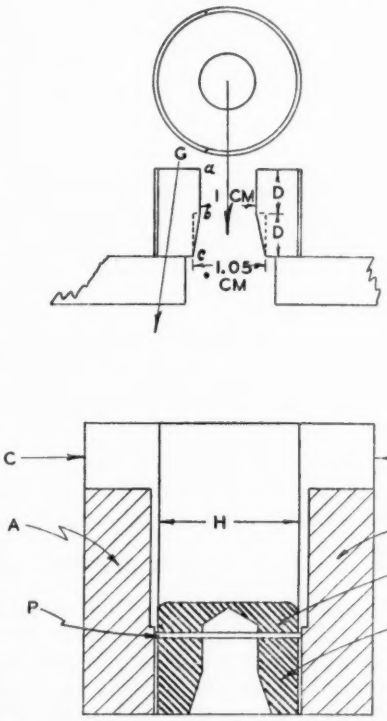

FIGURE 11.—*Details of diaphragm construction.*

There has been a tendency to use what we believe to be excessively thick diaphragms in the supervoltage X-ray region; for example, Mayneord [16] used a 3 cm thickness at 400 kv. We, therefore, made some measurements to determine the minimum lead thickness to stop

off 99.9 percent of the incident radiation. Accordingly, the diaphragms, constructed as shown in figure 11, were made of a thickness *2D*, where *D* is the thickness necessary to reduce the radiation to 1 percent of its incident value, and *2D* a thickness which will reduce the intensity to substantially less than 0.1 percent. From *a* to *b* the orifice is accurately cylindrical and from *b* to *c* it is tapered back to such a degree that the cross-sectional area at *c* is 10 percent greater than at *a* and *b*. Thus even had the lead been cut away, as indicated by the dotted lines, the diaphragm would not have permitted the passage, through its body, of more than 0.1 percent of the radiation passing through the orifice (assuming complete stoppage through G).

Values of *D* at different voltages were experimentally determined as shown in table 1:

TABLE 1.—*Required diaphragm thicknesses for different excitation voltages.*

Tube voltage	*D* (1%)	D (0.1%)
kv	mm	mm
240	3.4	6.0
300	5.5	9.2
360	6.7	12.0
400	8.2	16

Experience has also shown that to avoid distortion considerable care is required in the mechanical construction of the lead diaphragms. It has been found that a diaphragm held in a three-jaw chuck for the lathe operations will almost invariably distort after releasing, and use of a draw chuck does not usually permit a sufficiently accurate alignment of the hole. To make a diaphragm (*E*) we start with a solid block of brass through which a rough hole (*H*) is bored. This is partially filled with a hard lead alloy (Sb, Cd, Pb), which is forced into place with a rather high *steady* pressure (not hammer strokes). The block is then chucked at *C* and the portions *A*—*A* turned off. The lead (*E*) is then turned down to within about one or two thousandths of an inch of its finished size and cut off at *P*. After being allowed to age for a few days, a standard steel ball is gently forced back and forth through the opening to give it size as well as to burnish its surface.

6. SATURATION VOLTAGE

For the saturation voltage it was hoped to use direct current from a valve-rectified alternating-current source. However, after trying all the more common forms of voltage stabilization it was found to be impractical with the present very small capacity current-measuring system. Slow variations were not troublesome but irregular transients were. Several stabilizing devices which worked at a given voltage were impractical under the variable voltage requirements of our work. Large banks of radio *B* batteries were finally used.

IV. CURRENT MEASUREMENTS

The current measuring system is shown in figure 12.

The ionization current is amplified by means of an FP–54 electrometer tube in a balanced circuit of the type first described by Dubridge

and Brown [34]. The modification of the original Dubridge-Brown circuit shown was suggested to us by Dr. Leo Behr in 1934; this, in common with all modifications since suggested, was designed to minimize the difficulty of balancing the amplifier network, but unfortunately, at the expense of some of the stability inherent in the

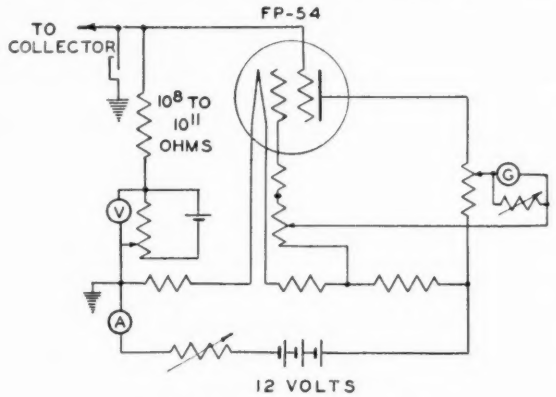

FIGURE 12.—*Amplifier circuit.*

original. With a galvanometer having a period of 3 sec and a current sensitivity of 5.7×10^{-9} amp/mm the voltage sensitivity of this system is 5.6×10^{-4} v/mm. With a grid resistor of $2.4\times10^{+9}$ ohms, the current sensitivity is 2.3×10^{-13} amp/mm; this sensitivity can be increased up to 50 times this value by increasing the grid resistance proportionately.

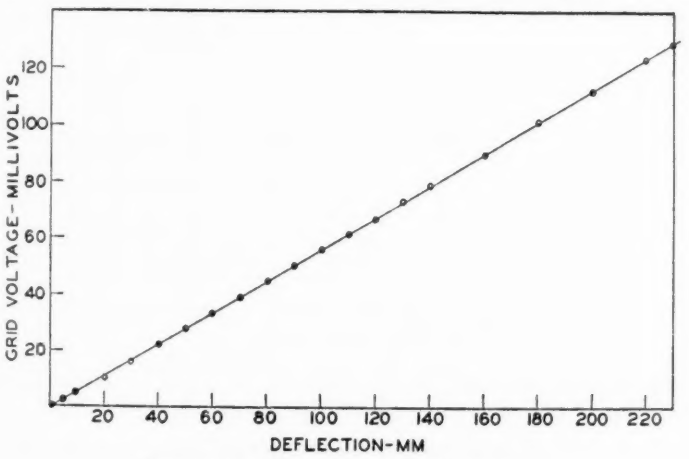

FIGURE 13.—*Amplifier calibration curve.*

The amplifier is linear to within 1 percent for deflections up to the maximum obtained, as is shown in figure 13.

Comparative current measurements are obtained by direct deflection; for absolute ionization-current measurements the system is used as a null measuring device. The voltage drop across the grid resistor is compensated by means of a potentiometer from the setting of which

the voltage drop across the grid resistor is determined. If the resistance of the grid resistor is known, the ionization current can be determined. The grid resistors are of the S. S. White type used in this laboratory in a variety of circuits during the past 5 years. Tests of these resistors made in connection with studies of X-ray ionization in liquids [35] has shown them to maintain their resistance values over long periods of time and have inspired confidence in their use. For absolute measurements, the grid resistor is calibrated by an electrostatic current compensator previously described [36], which is now used in the standarization of dosage meters.

The grid current of this amplifier is very small, being less than 10^{-4} times the ionization current measured; it is therefore possible to use this sytem as a null indicator in connection with an electrostatic compensator by simply removing the grid resistor.

The electrometer tube is shielded electrostatically and against radiation in a lead-covered cylindrical housing which is attached directly to the pressure ionization chamber. The tube proper is connected by means of a seven-wire shielded cable to the amplifier control panel, batteries, and galvanometer, all of which are placed inside the control room. The amplifier is remotely controlled by the observer from his station in the control room.

V. IONIZATION-CHAMBER CHARACTERISTICS

1. FIELD DISTORTION

In the 200-kv guarded-field ionization chambers it was found that even with guard wires there was a minimum permissible distance between wires and the chamber ends beyond which error would be introduced [30, 31]. It was desired to check this in the new

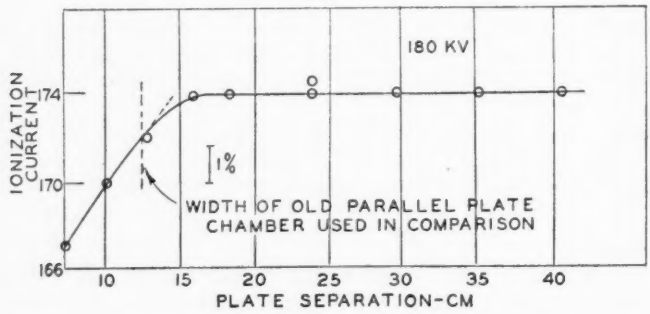

FIGURE 14.—*Curve showing effect of plate spacing on field distortion for 180-kv X-rays.*

chamber as well as to be certain that the field correction was adequate at all plate spacings.

Accordingly, the electrodes were placed as near as possible (10 cm) to the front of the chamber, set for a minimum separation and the guard wires disconnected from the system. Using an 8-mm beam of 180-kv X-rays the ionization current was measured for several plate spacings up to about 15 cm. Repeating this with the guard wires connected, no detectable difference was found. Measurements of

the ionization as a function of plate spacings (guard wires connected) are shown in figure 14. Definite saturation is reached at 15 cm, which spacing happens to be about the limit beyond which field distortion should normally be encountered for a 25-cm guard plate width, unless corrected with guard wires. That the curve is flat for spacings greater than 15 cm proves the efficacy of the guard-wire system.

Comparisons were made between this pressure standard and an early type of free-air standard designed for 180 kv [29]. (Mechanical difficulties prevented the use of our 200-kv guarded-field standard, which, however, agrees with the one used within 0.2 percent.) The same diaphragm and electrometer systems were used for both chambers so that the only factor entering the comparison was the effective plate length. Any further difference would have been due to such sources as spurious scattered radiation, stray ionization, etc. For a plate separation of 12 cm in the low-voltage standard, and 24 cm in the pressure standard, the latter indicated about 1.3 percent high. Referring to the curve in figure 14, it is seen that the 12-cm spacing in the old chamber is probably deficient by about 1 percent (as indicated by the ionization current). After making this 1-percent correction, the two chambers agree within the limits of experimental error.

2. SCATTERING FROM DIAPHRAGM AND PRESSURE-CHAMBER ENDS

The distance from the aluminim window at the front diaphragm to the collector electrode (in its closest position) is 59 cm, and while an effect of scattering from the thin aluminum entrant window upon the measured ionization seems unlikely, it was important to test therefor. In this connection, it may be stated that the indications of the chamber at high voltages will be unambiguous only if a state of electronic equilibrium exists in the region of the "ionized volume." "Mayneord's [3, 4] and Lauritsen's [5, 6] analyses of this problem are very clear and it is felt that their fundamental conditions for electronic equilibrium must be met.

To test for scattering from the entrant window, the collector was moved as close as possible to the fore end of the pressure chamber and measurements made with the aluminum window, first in the normal position (5 cm from the diaphragm) and then about 30 cm in front of the diaphragm. The indicated ionization was the same for both cases within limits of measurement. The same was true for similar tests made with a 0.5-mm copper window.

Further tests for scattering from the windows and for electronic equilibrium were effected by making ionization measurements at different positions of the collector plates along the length of the pressure chamber. The plate separation here was great enough to rule out any effect due to the beam divergence. Figure 15 shows a number of such curves at various excitation voltages. The 400-kv curve was made at a chamber pressure of 2 atm. It will be noted that all the graphs are linear within ± 0.5 percent or better, which agrees with the limits of accuracy at the time the measurements were made.

Scattering from the entrant window and diaphragm would show up as a sharp rise in the curve for small values of the distance between window and collector electrode. Similarly, scattering from the back of the chamber would cause a flattening of the curve at large values of the distance. Both are clearly absent. The linearity of the curves shows further that electronic equilibrium existed under all conditions of measurement.

Furthermore, from the slope of the curves may be directly obtained the air-absorption coefficients with which it is necessary to correct all measurements. It is to be expected that the curves of figure 15,

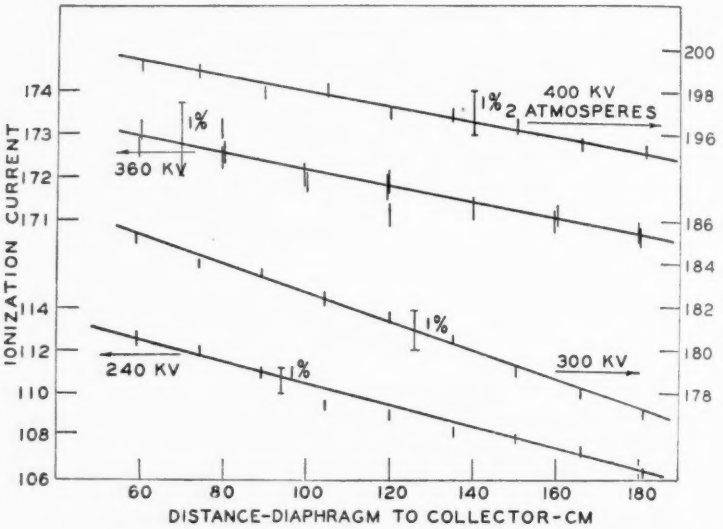

FIGURE 15.—*Curves showing the ionization as a function of the distance between front diaphragm and collector electrode.*

representing absorption of the X-ray beam by air, should be linear within the range studied, since the attenuation is only about 5 percent or less, and hence the change in quality is negligible. Air-absorption coefficients for several radiation qualities are listed in table 2. These may be compared with similar determinations made at lower voltages [37]. The application of air-absorption corrections becomes particularly important at elevated chamber pressures.

TABLE 2.—*Air-absorption coefficients*

Tube-voltage	Filter	Absorption per 100 cm of air	$\mu(cm^{-1})$
kv	mm	%	
240	1.2 Cu	4.77	48.8×10^{-4}
300	1.2 Cu	3.88	40.2
360	1.2 Cu+12 Al	1.50	14.9
400	1.2 Cu+12 Al	1.17	11.9

3. PLATE SEPARATION

To insure full utilization of the corpuscular emission from the air mass opposite the collector electrode, it is necessary to determine the minimum plate separation which will not cause a reduction in the measured ionization current. A number of such curves at different voltages are given in figure 16. It will be seen that the minimum spacing is very definite in all cases and increases rapidly with the X-ray excitation voltage. This is decidedly at variance with the investigations cited in the introduction [16, 17].

Particular attention is directed to the curves for 400-kv radiation. The curve at atmospheric pressure cannot be said to definitely reach a steady maximum even at the greatest possible plate separation of about 40 cm. However, under a chamber pressure of 2 atm the maximum is definitely reached at a plate separation of about 22 cm. This

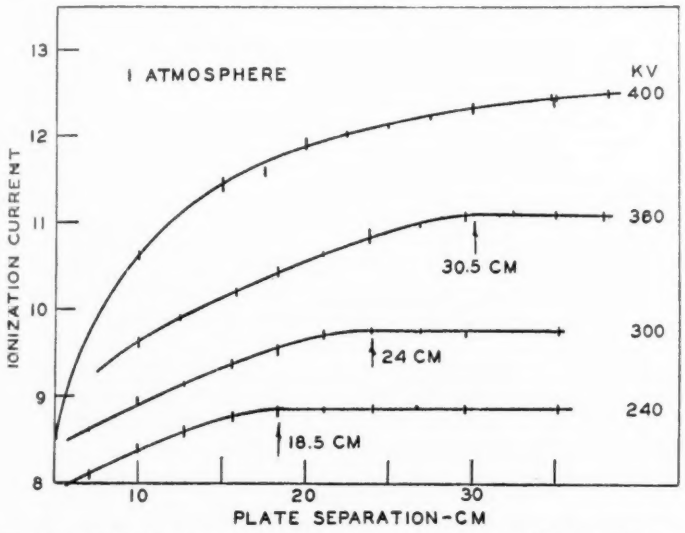

FIGURE 16.—*Ionization as a function of plate separation for different X-ray voltages.*

then fixes the working limits for the particular chamber. At atmospheric pressure, radiations up to 360 kv can be measured; above 360 kv elevated chamber pressures must be used. It is to be expected that a very considerable reduction in the size of the present chamber could be made by working at a pressure of 5 atm, but that has not been tested.

Failla [14], postulated the formation of an "electron cloud" to explain the limitation of his free-air ionization chamber in gamma-ray measurement. The possibility of a similar condition exists at 400 kv, where the scattering is predominantly in the forward direction and would show up as an apparent widening of the beam. This, in turn, would increase the necessary plate separation for electronic equilibrium as the collector-diaphragm distance is increased. Figure 17 shows several plate-separation curves made at 400 kv and 2-atm chamber pressure, for the different collector-diaphragm distances

shown. There is no evidence whatever of any cloud effect. Similar curves made at atmospheric pressure with 360-kv X-rays likewise showed no cloud effect. This proves only that the cloud effect did not influence the measurements under present conditions. It may well be that it does exist here in principle, and that equilibrium

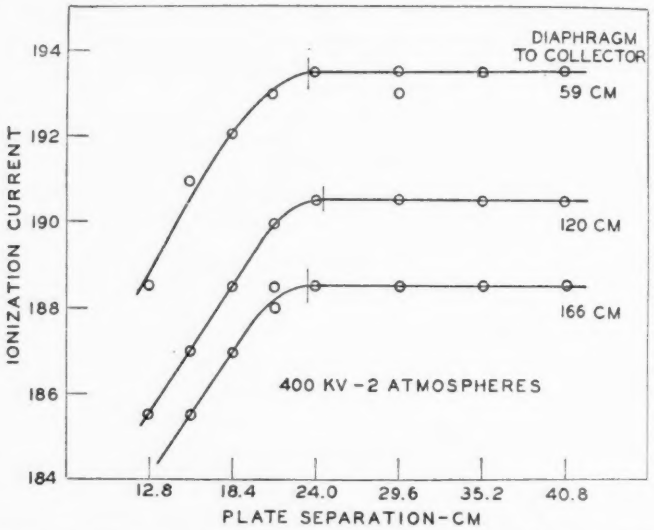

FIGURE 17.—*Ionization as a function of plate separation for different diaphragm-collector distances.*

obtained at our minimum distance of 59 cm. Such a condition, coupled with the fact that Mayneord and Jaeger used a much shorter diaphragm-collector distance than in our case, may contribute to the disagreement in the results.

4. SATURATION

In all of the preceding work, sufficiently high potentials were used across the ionization chamber to insure full or nearly full current saturation. Tests showed that saturation is apparently not as easily obtained as indicated in some earlier work of others. It should be pointed out that "saturation" is not necessarily a definite thing and depends upon the degree of accuracy to which the measurements are made. According to Thomson's theory [42], which has been shown to represent the facts fairly closely, the degree of saturation required will depend upon the precision sought, and the maximum potential will vary as the square root of the precision. Moreover, the potential required for a definite saturation is proportional to the current for the simple case of uniform ionization. While this condition does not obtain in the case of a standard ionization chamber, the saturation voltage does increase with the density of the ionization.

It is not to be expected that radiation quality changes within the range here used should have any great effect upon the shape of the saturation curve. This is shown to be the case in figure 18, which

gives a group of saturation curves for excitation voltages ranging from 200 to 400 kv, but in which the intensities at saturation were all

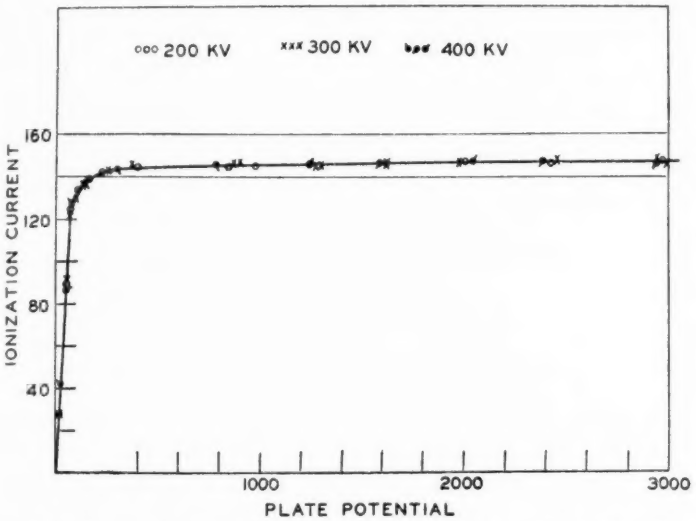

FIGURE 18.—*Saturation curves for plate spacing of 30 cm and different X-ray voltages.*

adjusted to the same value by moving the chamber away from the tube. It is clearly evident that within 0.5 percent all curves are alike and reach saturation at the same voltage.

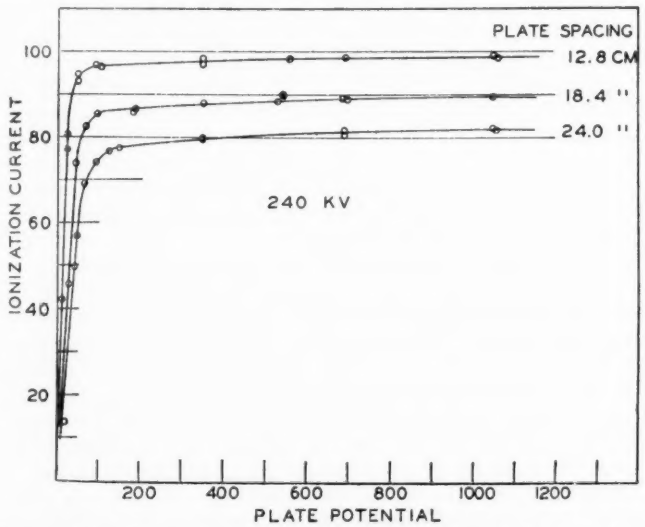

FIGURE 19.—*Saturation curves at 240 kv for different plate spacings.*

These curves may be compared with Mayneord's [16], which show saturation at 300 v for a 20-cm plate spacing, whereas our corresponding

spacing was 32 cm. The conditions are not exactly comparable, but we do not find his change in form of the curve below saturation. Referring to figure 18, it is seen that taking a value of 146 as representing saturation at 3,000 v, the chamber is within 10 percent of saturation at 90 v, 5 percent at 160 v, and 1 percent at about 1,000 v. Since our precision for the present measurements is about 0.5 percent, there is no need to employ more than about 2,000 v on the chamber. This lack of saturation at low voltages is also evident in figure 19, which gives similar curves for smaller plate spacings.

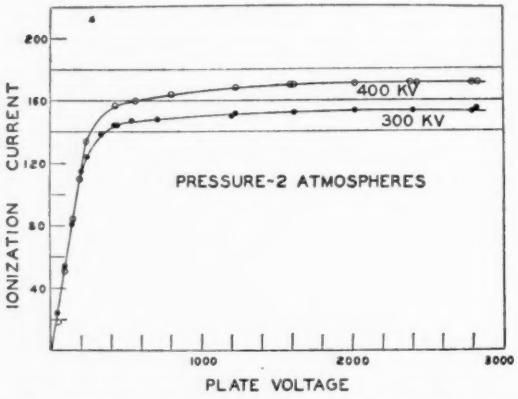

FIGURE 20.—*Saturation curves at 2 atmospheres.*

A third set of saturation curves (fig. 20) was made at a chamber pressure of 2 atm. Again, taking the current at 3,000 v as saturated, the ionization chamber is within 10 percent of saturation at 400 v, 5 percent at 900 v, and 1 percent at about 2,000 v. These results show the requirement of an approximate doubling of the saturation voltage at double the pressure, as might be expected.

5. IONIZATION MEASUREMENTS AT ELEVATED PRESSURES

Measurements already discussed have shown that the ionization chamber behaves normally, at slightly elevated pressures, with respect to plate separation, saturation, and electronic equilibrium. It remains, therefore, to insure that the ionization chamber actually measures all the ions produced at higher chamber pressures. Above 8 or 10 atm Zanstra has shown that there is a definite loss of ions through volume or columnar recombination [40], so that the true ionization can only be inferred by applying the special methods devised by either Mohler and Taylor [41] or Zanstra [40].

An accurate check of the possible loss has been made up to 3.3-atm pressure. Figure 21 shows the ionization current as a function of the pressure in centimeters of mercury, the lower curve giving the current as actually measured. However, air absorption is relatively large and increases with pressure, so that this curve must be corrected for absorption between the diaphragm and collector, using the absorption data obtained from table 2. The corrected curve is then seen to be a straight line within experimental errors. Accordingly, we may conclude that at least up to pressures of 3.3 atm there is no appreciable loss of ionization because of recombination. This is in agreement with the recent work by Tanaka [38] at lower excitation voltages.

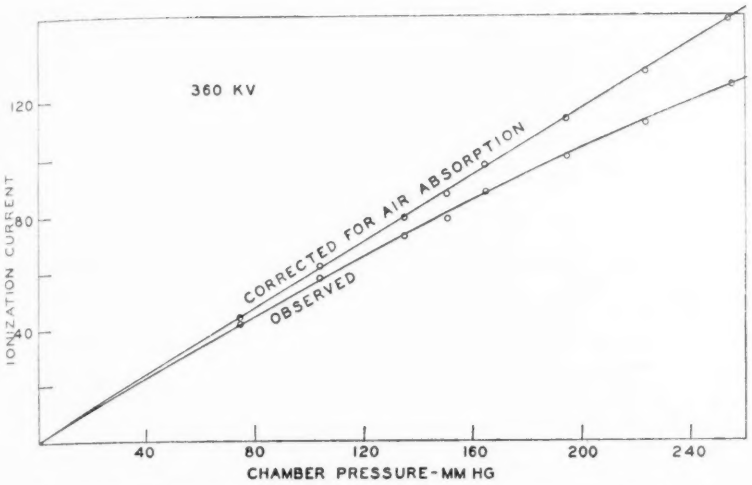

FIGURE 21.—*Ionization current as a function of air pressure in chamber.*

6. INVERSE-SQUARE LAW

Application of the inverse-square law was tested for distances between target and chamber diaphragm ranging from 2.5 to 5.5 m. For this the chamber diaphragm was 1.5 cm and the tube diaphragm 4 cm in diameter. The results after correction for air absorption show close adherence to the inverse-square law, so that when necessary we may use it as a basis in calibration work.

VI. GENERAL CONCLUSIONS

From the measurements described above, we may conclude that it is feasible to construct a standard free-air ionization chamber for the measurement of supervoltage X-rays, although our basis for this conclusion rests upon physical factors which differ decidedly from those of Jaeger [17], who reached the same conclusion. In particular, it is found to be possible to measure radiations of excitation potentials up to 360 kv with a free-air chamber of moderate plate separation (30 cm) at atmospheric pressure. For higher excitation voltages the ionization chamber may be kept within practical size limits by using it at slightly elevated pressures.

It appears, from these results, possible to construct an ionization chamber of very much smaller dimensions than herein used. Our own chamber was made its present size to permit the unhampered exploration of supervoltage measurements up to well over a million volts and possibly into the gamma-ray region. The results thus far indicate fair promise for extension to higher excitation voltages than used here.

Through the use of specially constructed X-ray generating equipment it is possible to make free-air ionization measurements in the supervoltage region with an accuracy comparable with that obtained in the high- and low-voltage region. There is thus provided a means for measuring the international roentgen by a means wholly inde-

pendent of the thimble chamber and against which the thimble-chamber measurements may be compared. It is, therefore, possible to calibrate the clinical dosage meter under the same conditions as obtain for lower voltage radiations.

Some preliminary comparisons with thimble chambers yield reasonable results, but their description will be reserved until such later time as they may be carried out more fully.

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PREPARATION AND APPLICATION OF CHROMOUS SOLUTIONS FOR THE ABSORPTION OF OXYGEN IN VOLUMETRIC GAS ANALYSIS

By Joseph R. Branham

ABSTRACT

The reaction between acidified and nonacidified solutions of chromous chloride or of chromous sulfate with oxygen was studied and found to be complete (±0.02 percent). Acidified solutions of chromous sulfate evolve hydrogen sulfide and should not be used for volumetric analysis over mercury. Acidified solutions of chromous chloride evolve small amounts of hydrogen. The errors caused by this hydrogen are of the same order of magnitude as those caused by the formation of carbon monoxide when oxygen is determined by absorption in alkaline potassium pyrogallate. The displacement of dissolved nitrogen from the chromous solutions, particularly chromous sulfate, and the subsequent partial re-solution of this nitrogen may cause low apparent percentages of oxygen in the samples to be reported. Alkaline potassium pyrogallate and concentrated acidified solutions of chromous chloride should be used to determine oxygen volumetrically, in preferenee to the more dilute solutions of chromous sulfate prepared by reduction of saturated solutions of potassium chromic sulfate.

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I. INTRODUCTION

Many chemists have suggested that the reaction between oxygen and solutions which contain either chromous chloride or chromous sulfate be used to determine the oxygen content of gas mixtures by the methods of volumetric gas analysis.[1]

The advantages claimed for these solutions are great speed of reaction and the selective chemical absorption of oxygen from gas mixtures which contain carbon dioxide.

[1] Otto von der Pfortden first proposed the use of chromous chloride for this purpose. Liebigs Ann. Chem. 228, 112 (1885). Anderson and Riffe examined the reaction between acidified and nonacidified solutions of chromous chloride and oxygen and reported that the first of these reagents evolved too much hydrogen to be used in volumetric gas analysis, while the second did not absorb all of the oxygen in the gas samples. J. Ind. Eng. Chem. 8, 24 (1916). Hosmer W. Stone and Charles R. Dixon, at the Rochester meeting of the American Chemical Society in September 1937, suggested that acidified and nonacidified solutions of chromous sulfate might be used to determine oxygen volumetrically.

When the oxygen in mixtures of gas containing oxygen and nitrogen is determined volumetrically, it is customary, and for exact work necessary, to absorb the oxygen in a reagent which is saturated with nitrogen at the beginning and end of each analysis. The amount of oxygen reported is the difference between the volumes of gas in the apparatus before and after the sample has been passed through the reagent. The apparent percentage of oxygen in the sample will therefore depend not only on the volume of oxygen which reacts, but also on the volume of nitrogen or any other gas that is absorbed by or displaced from the reagents during the analysis.

For these reasons solutions of chromous sulfate and chromous chloride were examined with reference to: (1) Completeness of the reaction between them and oxygen; (2) formation and subsequent liberation of hydrogen; (3) formation and subsequent liberation of hydrogen sulfide; and (4) physical solution and displacement of nitrogen from these reagents during the chemical absorption of oxygen.

II. PREPARATION OF SOLUTIONS

The chromous solutions used in this study were prepared either from violet chromium potassium sulfate or from green chromic chloride by reduction with amalgamated zinc. The solubilities of these two salts are approximately 0.4 and 4.0 moles per liter; and the latter salt was used when concentrated solutions of chromous chloride were prepared. Solutions containing green chromic chloride are not appreciably reduced by amalgamated zinc unless an excess of hydrochloric acid is present. Neutral [2] solutions of chromous chloride were prepared by adding an excess of barium chloride to solutions of neutral chromous sulphate and filtering off the barium sulphate which precipitated, all operations being performed under an atmosphere of nitrogen.

The solutions of chromous sulfate were prepared from chromium potassium sulfate by reduction with amalgamated zinc in a Jones reductor. Nitrogen was substituted for the carbon dioxide used by Stone and Beeson [3] to force the solutions through the reductor. It was necessary to reduce the green chromic chloride in an Erlenmeyer flask nearly full of amalgamated mossy zinc, because the Jones reductor containing 20-mesh zinc was clogged by a precipitate under these conditions. The time required for the reduction of the green chloride in the flask was greater than that for the reduction of the chromium potassium sulfate in the Jones reductor, but required no great amount of attention. Nitrogen was bubbled through the solutions prepared from chromic salts by reduction with amalgamated zinc, in order to free them from dissolved hydrogen and to saturate them with nitrogen (in accordance with normal volumetric procedure) before they were transferred to the absorption pipettes.

III. EVOLUTION OF HYDROGEN SULFIDE FROM CHROMOUS SOLUTIONS

All of the solutions of chromous chloride and of chromous sulfate prepared in the earlier stages of this work evolved hydrogen sulfide. Very low concentrations of this gas react with the mercury in the

[2] This term is used throughout this paper to denote aqueous solutions to which no acid was added.
[3] Ind. Eng. Chem. Anal. Ed. 8, 188 (1936).

burette and manometer of a volumetric gas-analysis apparatus, and, by altering the shape of the menisci, prevent accurate volumetric measurements.[4] The presence of hydrogen sulfide was established by bubbling nitrogen through the solutions and passing the exit gas over paper moistened with lead acetate or over the clean surface of mercury.

There are at least three ways by which the chromous solutions may be contaminated with hydrogen sulfide. These are: (1) From combined sulfide and possibly sulfate as impurities in the zinc used to reduce the chromic salts; (2) from the sulfur compounds as impurities in liquid petrolatum when this is used to prevent contact between the free surface of the chromous solutions and the atmosphere in the open arm of an absorption pipette; and (3) by reduction of the sulfate radical in the presence of sulfuric acid and bivalent chromium.

Samples of mossy, stick, and "20-mesh" zinc from freshly opened containers evolved hydrogen sulfide when treated with dilute hydrochloric acid. The concentration of this gas was greatest during the first acid treatment and diminished when the zinc was washed and fresh portions of acid were added to the flask. Three or more 10-minute reactions with fresh acid were necessary before the zinc was sufficiently pure to be amalgamated and used to produce chromous solutions free from hydrogen sulfide. Zinc treated in this way, before being amalgamated by treatment with mercuric chloride, produced neutral solutions of chromous sulfate and acid solutions of chromous chloride which did not evolve detectable amounts of hydrogen sulfide during the period covered by the tests.

The evidence concerning the presence or absence of hydrogen sulfide and also of hydrogen in the neutral solutions of chromous sulfate is not completely satisfactory. Both hydrogen and hydrogen sulfide were displaced from some of the neutral solutions of chromous sulfate when relatively long periods elapsed between their use in analyses. On the basis of the volumes of nitrogen which had been passed through these solutions during the analyses performed prior to the period during which the reagent was idle all of the hydrogen or hydrogen sulfide in the reagent by reason of the method of preparation should have been displaced. It appears quite probable therefore that both hydrogen and hydrogen sulfide are generated slowly by this reagent.

When hydrogen sulfide-free solutions of chromous chloride acidified with hydrochloric acid were stored under a layer of liquid petrolatum, to protect them from direct contact with air at their open surface in the atmospheric arm of an absorption pipette, they became contaminated with hydrogen sulfide. The amount of hydrogen sulfide displaced from the solutions under these conditions was small, but sufficient to gradually blacken the mercury in the volumetric apparatus and, in time, to impair the accuracy of the volumetric determinations. Hydrogen sulfide from this source was eliminated by substituting an atmosphere of nitrogen for the layer of liquid petrolatum in the open arm of the absorption pipettes.

The reduction of sulfur compounds in liquid petrolatum to hydrogen sulfide was confirmed in the following manner. An acid solution of chromous chloride was prepared and equal volumes of it were put

[4] According to H. A. Bright, of this Bureau, the extremely small amount of hydrogen sulfide which prevents the accurate determination of gas volumes over mercury is of negligible consideration in titrimetric or gravimetric methods employing zinc and acid for reduction.

into two gas-washing bottles. Liquid petrolatum was added to one of these and a current of nitrogen passed through the two bottles in series. Tests with lead acetate papers showed that the exit gas from the bottle containing the chromous solution in contact with liquid petrolatum contained hydrogen sulfide. This test was negative in the case of the bottle which contained only chromous chloride.

Attempts to prepare acid solutions of chromous sulfate which were free from hydrogen sulfide were unsuccessful. Experimental evidence of the reduction of the sulfate radical to hydrogen sulfide by bivalent chromium in the presence of sulfuric acid was obtained as follows:

1. The absence of hydrogen sulfide in a solution of chromous chloride, containing hydrochloric acid, was established by passing nitrogen through it and then over lead acetate paper. No lead sulfide was formed. This test was then repeated after the addition of sulfuric acid to the chromous solution. The paper darkened almost immediately.

2. One-fourth of a single sample of a neutral chromous sulfate solution was put into each of four gas-washing bottles, three of which contained measured volumes of sulfuric acid. These bottles were connected in series, the first being neutral, while the second, third, and fourth contained sufficient sulfuric acid to make them 0.1, 1.0, and 5 *N*. Lead acetate papers were put in the exit connection of each bottle and nitrogen was passed through them. The lead acetate paper placed in the exit gas from the neutral solution showed only a trace of color after a long exposure, but the papers exposed to the gas which had passed through the acid solutions darkened in a few minutes.

IV. APPARATUS AND PROCEDURE

Volumetric measurements were made over mercury in the gas-analysis apparatus previously described.[5] The calibration of the burette permitted volumes to be estimated to 0.01 ml and readings by independent observers rarely differed more than 0.02 ml. This does not necessarily mean that gas volumes were determined accurately within ± 0.02 ml, but rather that the apparent volume of the gas, which may or may not have been the correct volume, was repeatedly observed within these limits. This apparatus is equipped with a mercury-filled manometer, between the burette and compensator, one side of which is in contact with the gas being measured The reaction between oxygen and the chromous solutions took place in one of two Schott & Genossen pipettes.[6] These were equipped with distributor tips of sintered glass of porosity grade G2. The solution in the atmospheric arm of the pipette containing a chromous solution was protected from contact with air by connecting its atmospheric arm with an extra pipette which contained alkaline potassium pyrogallate. The open surface of the chromous solutions was thereby maintained under an atmosphere of nearly pure nitrogen. A layer of liquid petrolatum was used to prevent direct contact between the potassium pyrogallate and the atmosphere.

The volumetric apparatus was also equipped with a slow-combustion pipette and an absorption pipette containing alkaline potassium

[5] Martin Shepherd, BS J. Research **6**, 121 (1931) RP266.

[6] These pipettes are listed as 153–SG2 on page 18 of the catalog of the Fish-Schurman Corporation of New York City.

pyrogallate.[7] The combustion pipette was used in the determination of the hydrogen evolved by the chromous solutions during the absorption of oxygen. The residual gas after reaction with the chromous solutions was passed through potassium pyrogallate to determine the completeness of the reaction between oxygen and the chromous solutions.

Mixtures of oxygen and nitrogen for analysis were taken from two sources. These were: (1) Air, drawn from outside of the building by means of a copper tube and freed from carbon dioxide by passage through ascarite; and (2) a cylinder of commercial oxygen obtained by rectification of liquid air.[8] This oxygen contained no measurable amounts of carbon dioxide or combustible gases.

When commercial oxygen was analyzed, by absorption in the chromous solutions or in potassium pyrogallate, a measured volume of nitrogen (to serve as a carrier gas) was stored in the absorption pipette above the solution before the oxygen in the sample was absorbed. This nitrogen was needed in the latter stages of an absorption to carry the last portions of unabsorbed oxygen through the solutions in the pipettes, and to saturate the reagent with nitrogen at the end of each analysis. The difference between the volume of nitrogen which was stored at the beginning of an analysis and that left at the end of the analysis is the apparent "nitrogen" or inert content of the sample.

V. COMPLETENESS OF THE REACTION BETWEEN OXYGEN AND CHROMOUS SOLUTIONS

R. P. Anderson and J. Riffe[9] investigated the reaction between oxygen and a neutral solution of chromous chloride. They reported that this solution will absorb only about 97 percent of the oxygen in air. They also found that acidified solutions of chromous chloride liberate sufficient hydrogen to make them unsuitable for use in volumetric gas analysis.

The results obtained by Anderson and Riffe were not confirmed in the present study. Repeated tests showed that the gas which remained after air or commercial oxygen had reacted with acid or neutral solutions of either chromous chloride or chromous sulfate underwent no measurable change of volume when passed through potassium pyrogallate. The absence of measurable volumes of oxygen in the gas which remained after oxygen had reacted with acid chromous chloride, which evolved some hydrogen, was also shown by the absence of a contraction when this gas was passed over a heated platinum spiral in the slow-combustion pipette.

[7] This solution was prepared by adding 15 g of pyrogallic acid dissolved in 10 ml of hot water to each 100 ml of a solution which was saturated with potassium hydroxide at room temperature. There is a possibility that some of the hydroxide solutions used were not completely saturated because of lack of stirring, even though there was an excess of the solid present. This may account in part for the relatively large amounts of carbon monoxide found in the gas which remained after oxygen (approximately 99 percent) was absorbed by several batches of alkaline potassium pyrogallate. For the preparation and use of this reagent see: R. P. Anderson, J. Ind. Eng. Chem. **7**, 587 (1915).

[8] This oxygen was of higher purity than is usual, owing to especial precautions taken by the Southern Oxygen Company of Washington, D. C., in the operation of the air rectifier and in filling the cylinder.

[9] J. Ind. Eng. Chem. **8**, 24 (1916). The chromous chloride used by these investigators was prepared by reducing violet chromic chloride in a current of hydrogen at 400 to 500° C. The reduced salt was dissolved in water and used to absorb oxygen. The completeness of the reaction between oxygen and this solution was measured by shaking air and chromous chloride together in a contact pipette and then treating the residual gas with potassium pyrogallate. The treatment of the residual gas with potassium pyrogallate increased the apparent oxygen content of air from about 20.3 to 20.95 percent. These investigators did not definitely identify the gas absorbed by potassium pyrogallate as oxygen, and there is a possibility that the reaction between oxygen and the chromous solution was complete but was accompanied by the liberation of carbon dioxide or some other acid gas from the solution. (See RP 1113. Displacement of nitrogen from and its solution in certain reagents. J. R. Branham and Max Sucher.)

VI. EVOLUTION OF HYDROGEN FROM CHROMOUS SOLUTIONS AND OF CARBON MONOXIDE FROM ALKALINE POTASSIUM PYROGALLATE

The hydrogen or carbon monoxide evolved from the reagents during analyses was determined by slow combustion in the presence of an excess of oxygen. The hydrogen was calculated from the contraction and the oxygen consumed; and the carbon monoxide from contraction, oxygen consumed, and carbon dioxide formed. Carbon monoxide was also determined in one instance by reaction with iodine pentoxide.[10] The error introduced into the apparent percentages of oxygen by the evolution of hydrogen is of the same order of magnitude as the similar error introduced by the formation of carbon monoxide during the determination of oxygen by absorption in alkaline potassium pyrogallate. It is probable, however, that the amount of hydrogen displaced from the acidified solutions of chromous chloride will increase if the solution stands idle for long periods. This will cause serious errors unless the dissolved hydrogen is swept out of the reagent by nitrogen before it is used to determine oxygen. This sweeping out is not necessary with alkaline potassium pyrogallate because the carbon monoxide displaced from this reagent is supposedly formed only during the absorption of oxygen.

The amounts of hydrogen or of carbon monoxide evolved by the reagents during the analysis of a single 80-ml sample of commercial oxygen were too small to be determined precisely by slow combustion. Therefore, the nitrogen which was used as a carrier gas was not discarded after each analysis but was used over and over again during the entire series of analyses which were made with each portion of reagent. The concentration of hydrogen or of carbon monoxide was thereby increased and could be determined somewhat more accurately than would otherwise have been possible. Even under these conditions, however, the combustion analyses were not very satisfactory. Calculations of the amounts of hydrogen based on the contraction or the amounts of oxygen consumed were not in good agreement, and the amounts of carbon monoxide calculated from the contraction, the oxygen consumed, or the carbon dioxide formed did not agree closely with each other.

This disagreement may have resulted from volumetric error (the volumes involved were small), or from the presence of small amounts of combustibles other than hydrogen or carbon monoxide. The disagreement, while apparently significant, is not serious with respect to the actual amounts of gas involved; and a selected average may be used to make approximate corrections of the analytical results.

The amount of hydrogen in the carrier gas (combined residues) from analyses 1, 2, and 3 (table 4), after the absorption of oxygen by neutral chromous sulfate, was determined by slow combustion. This amount when calculated from the contraction was 0.22 ml and when calculated from the oxygen consumed was 0.32 ml. The 0.11 percent of hydrogen reported in these analyses is based on the average of these calculations. A similar examination of the carrier gas from

[10] The author is indebted to E. Carroll Creitz of this Bureau for this determination.

analyses 4 to 7, inclusive, (table 4) resulted in no hydrogen being found. An examination of the two portions of carrier gas from analyses 8 to 12, inclusive, and 17 to 19, inclusive, indicated amounts of hydrogen so small that its presence is not definitely established.

The amount of carbon monoxide in the carrier gas from analyses 18 to 25, inclusive, table 2, was determined by slow combustion. The amount of carbon monoxide calculated to be present was 0.80 ml from the contraction, 0.68 ml from the oxygen consumed, and 0.60 ml from the carbon dioxide formed. The average of these values corresponds to an 0.11 percent correction for CO.

Since this amount is approximately three times as great as the amount usually found after analyses of this type, a similar portion of this carrier gas was examined by reaction with iodine pentoxide. The correction for carbon monoxide based on this analysis is 0.07 percent; and as this method of determining small amounts of carbon monoxide is more accurate than slow combustion, this correction is reported in table 2. It is possible that the correction calculated from the results of the slow combustion analysis indicates the presence of combustibles other than carbon monoxide in the carrier gas.

The neutral solution of chromous sulphate used in the series of analyses which resulted in the evolution of 0.27 ml of hydrogen (average of 0.22 ml and 0.32 ml) had been treated as follows before the series of analyses was made and the hydrogen evolved.

(1) 89 ml of nitrogen was passed through the freshly prepared solution 10 times and discarded.

(2) 69 ml of nitrogen was passed through the reagent 10 times and discarded.

(3) 62 ml of nitrogen was passed through the reagent 4 times and discarded.

(4) 63 ml of nitrogen was passed through the reagent 4 times and discarded.

(5) 63 ml of nitrogen was passed through the reagent 4 times and discarded.

(6) 67 ml of nitrogen was passed through the reagent 4 times and discarded.

(7) 62 ml of nitrogen was passed through the reagent 4 times and discarded.

The reagent then remained idle for 3 days and was used for the analyses of oxygen here reported.

Previous experience indicates that all of the dissolved hydrogen originally in this reagent should have been swept out by the nitrogen which had been passed through it. The most probable explanation for the hydrogen which was found in the carrier gas after the oxygen analyses is that it was formed by reduction of water by bivalent chromium or else that minute pieces of zinc passed through the glass wool filter of the Jones reductor and produced hydrogen in the absorption pipette. The evolution of hydrogen sulfide from neutral solutions of chromous sulfate when the solutions had remained idle for long periods was mentioned in section III. A similar slow evolution of hydrogen may, therefore, be possible.[11]

[11] A list of references regarding the possible evolution of hydrogen from solutions of chromous sulfate is given by Stone and Beeson, footnote 3. A list of references concerning the evolution of hydrogen from solutions of chromous chloride is given by R. P. Anderson and J. Riffe, footnote 9.

VII. DISPLACEMENT OF NITROGEN FROM CHROMOUS SOLUTIONS DURING ANALYSES

Measurable volumes of nitrogen were found to be displaced from the chromous solutions by the passage of unabsorbed oxygen through them. These amounts were measured by making the first passage of 80-ml samples of oxygen through the chromous solutions and then removing the oxygen which had not reacted, by repeated passages of the gas which remained through alkaline potassium pyrogallate. The differences between the volumes of nitrogen which remained after these analyses, and the volumes which remained after analyses by absorption in alkaline potassium pyrogallate alone, were assumed to be a measure of the nitrogen displaced from the chromous solutions. The amounts of nitrogen which were displaced from the chromous solutions were found to increase rapidly as the concentration of the chromous solutions decreased during successive analyses. Measurements made with 260 ml of a neutral solution of chromous sulfate showed that the amount of nitrogen which was displaced was 0.14 ml when the solution was 0.4 *M*, and 0.74 ml when the solution was 0.1 *M*. Similar measurements indicated that the amounts of nitrogen displaced from chromous chloride were seldom greater than 0.1 ml unless the concentration of the chromous salt fell below 0.5 *M*.

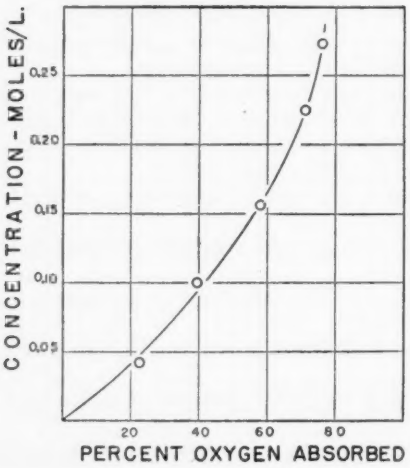

FIGURE 1.—*Percentage of oxygen absorbed in a single passage of 80-ml samples of commercial oxygen through neutral solutions of chromous sulfate.*

The measured amounts of oxygen which reacted chemically in this particular apparatus during the first passage of 80-ml samples of commercial oxygen through 220 ml of chromous sulfate are given in figure 1. These amounts are plotted against the calculated molality of the chromous sulfate. Similar measurements made with 0.88 and 2.2 *M* solutions of chromous chloride indicated that 80 to 95 percent of the oxygen in an 80-ml sample of commercial oxygen reacted during the first passage.

A part of the nitrogen which is displaced from the chromous solutions during the first passages of the samples through them will be redissolved during the latter part of the analyses by repeated passages of nitrogen through the reagents. The difference between the amounts redissolved in this way and those which were displaced may be large under certain conditions and constitute the principal source of error when these solutions are used in volumetric gas analysis.

Several variable conditions in the system prevent the re-solution of exactly the same amounts of nitrogen during the latter passages as

were displaced during the first passages. The first of these variables is the change of solubility of nitrogen in the reagent caused by the rise of temperature of the reagent which occurs when oxygen reacts. This rise of temperature when 80-ml samples of oxygen reacted under the conditions of these analyses was measured by a thermometer immersed below the surface of the reagents in the atmospheric arm of the absorption pipettes. The maximum observed temperature rises were 3.4, 2.6, and 1.4° C when the oxygen reacted with 220 ml of chromous sulfate, chromous chloride, and alkaline potassium pyrogallate, respectively.

The maximum temperature rise was usually registered after the fourth passage of the sample through the reagent. Thereafter, the reagent was cooled slowly by loss of heat to the room and by the nitrogen passing through it. After the tenth passage of the sample and nitrogen through the solution of chromous chloride, the temperature of the reagent had fallen about 0.7° C below the maximum, so that the temperature at this time was 1.9° C above the initial temperature.

The changes of solubility of nitrogen with temperature in 220 ml of 0.4 *M* chromous sulfate, 4 *M* chromous chloride (acidified) and alkaline potassium pyrogallate are reported in RP1113 to be approximately 0.025, 0.01, and 0.003 ml/°C respectively. On the basis of these temperature coefficients and the observed rise of temperature of the reagents, amounts of nitrogen which may approach 0.08, 0.03, and less than 0.01 ml of the nitrogen displaced during the first passages of oxygen through these reagents will not be redissolved unless the reagents are brought to the temperature which prevailed before the oxygen was absorbed. This precaution was not taken when the data given in tables 1, 2, and 3 were obtained and the change of temperature of the reagents was not then measured.

Two other possible causes of error in the analytical results are: (1) That an insufficient volume of nitrogen or an insufficient number of passages of nitrogen were made during each analysis to resaturate the reagents with nitrogen; and (2) that measurable volumes of nitrogen dissolved through the open surface of the reagents in the atmospheric arm of the pipettes, after the first passages of the sample of oxygen through the reagents, at which time the reagent is relatively unsaturated with respect to nitrogen. This would prevent a like amount of nitrogen which has been displaced from the reagent from redissolving in it during the latter passages of nitrogen.

These two sources of error were studied and are reported in RP1113. This report indicates that the reagents used to absorb oxygen should have been substantially saturated (± 0.02 ml) with nitrogen when six or more passages of 60 ml of nitrogen were made during the analyses of samples of commercial oxygen. It also indicates that small but measurable amounts of nitrogen may have dissolved through the open surface of the chromous solutions in the atmospheric arm of the absorption pipette when these reagents were used to absorb commercial oxygen.

VIII. RESULTS OF ANALYSES OF MIXTURES OF OXYGEN AND NITROGEN

The results of analyses when samples of carbon dioxide-free air and of commercial oxygen were analyzed by absorption in solutions of chromous chloride, chromous sulfate, and alkaline potassium pyrogallate are reported in this section.

The chromous solutions used in these analyses were substantially saturated [12] with nitrogen and supposedly free from dissolved hydrogen prior to the start of the first analysis of each series. The open surface of the chromous solutions in the atmospheric arm of the absorption pipettes was in contact with an atmosphere of nitrogen, maintained as described in section IV. The amounts of dissolved nitrogen in these reagents at the start of the analysis following the first of a given series depended upon the amounts which had dissolved during the previous analyses, and upon the amounts which dissolved through the open surface of the reagents in the atmospheric arm of the absorption pipettes during the period between analyses.

The concentrations of the chromous solutions given in the tables are the initial concentrations at the start of each series of analyses. These concentrations were determined by pipetting aliquot parts into an excess of potassium dichromate solution and determining the excess of dichromate by titrating potentiometrically with ferrous sulfate.[13]

The values used to express the precision of the average results are the average of the arithmetical deviations of the separate results from the mean value of each series of analyses. The variation between the individual results is somewhat greater than would be expected from the reproducibility with which a fixed volume of gas can be measured in the apparatus.

The results of the analyses of carbon dioxide-free air are given in table 1. The average results obtained with alkaline potassium pyrogallate and with the concentrated solutions of chromous chloride (acidified) are in good agreement with each other and with the generally accepted value of the average percentage of oxygen in air. The average results obtained with the dilute solutions of chromous chloride (acidified) and of chromous sulfate (neutral) indicate a lower apparent percentage of oxygen. These low results are attributed to the transfer of nitrogen and possibly of some hydrogen from the reagents to the gas which remained after the removal of oxygen. It is also barely possible that since the removal of oxygen can be established in this apparatus only to ± 0.02 ml, the low results may have been caused in part by a trace of oxygen in the residual gas. This supposition, however, is extremely improbable in view of the fact that the more concentrated solutions of chromous chloride give results which are in excellent agreement with those obtained with alkaline potassium pyrogallate.

The results of the analyses of the "air-separated" oxygen, by absorption in alkaline pyrogallate, in concentrated chromous chloride (acidified) or in 0.4 *M* chromous sulfate (neutral) are reported in tables 2, 3, and 4.

[12] The solubility of nitrogen at room temperature in 220-ml portions of chromous sulfate, chromous chloride, and alkaline potassium pyrogallate is reported in RP1113 as approximately 2.0, 0.9, and less than 0.2 ml, respectively.

[13] This work was done by John L. Hague of this Bureau.

TABLE 1.—*Apparent percentages of oxygen in air as determined with different reagents*

Analysis	Reagent									
	Potassium pyrogallate		2.2 *M* $CrCl_2$ (acid)		0.88 *M* $CrCl_2$ (acid)		0.25 *M* $CrCl_2$ (acid)		0.4 *M* $CrSO_4$ (neutral)	
	Oxygen found	Number of passages	Oxygen found	Number of passages	Oxygen found	Number of passages	Oxygen found	Number of passages	Oxygen found	Number of passages
	%		%		%		%		%	
1	20.88	4	20.92	2	20.92	2	20.92	2	20.99	6
2	20.95	4	20.91	3	20.98	2	20.92	2	20.87	6
3	20.98	4	20.96	4	20.95	2	20.88	3	20.87	6
4	20.93	4	20.93	2	20.89	2	20.91	3	20.94	6
5	20.96	4	20.99	3	20.92	2	20.93	2	20.84	6
6	20.94	4	20.96	4	20.98	2	20.90	3	20.86	6
7	20.92	4	20.94	2	20.94	2	20.92	3	20.94	3
8	20.88	4	20.87	3	20.96	2	20.92	3	20.88	6
9	20.96	4	20.96	4	20.94	2	20.91	2	20.90	3
10	20.93	4	20.87	2	20.91	2	20.92	2	20.88	3
11	20.88	4	20.88	3	20.94	2	20.93	2	20.94	4
12	20.94	4	20.87	4	20.93	2	20.90	2	20.90	14
13	20.92	4	20.86	2	20.95	2	20.87	3	20.90	14
14	20.89	6	20.91	3	20.94	3	20.88	2	20.94	4
15	20.96	6	20.93	4	20.96	3	20.88	3	20.90	4
16	20.97	6	20.90	3	20.93	3	20.93	3	20.90	4
17	20.96	6	20.93	4	20.94	3	20.88	3	20.86	4
18	20.89	6	20.94	4	20.97	3	20.91	7	20.90	4
19	20.95	6	20.90	4	20.91	3	20.93	5	20.92	4
20	20.91	6	20.95	4	20.95	3	20.91	3	20.91	4
21	20.92	6	20.94	4	20.96	3			20.86	4
22	20.92	6	20.93	4	20.96	3			20.87	8
23	20.95	6	20.94	4	20.95	3			20.80	6
24	20.92	6			20.96	3			20.95	8
25	20.98	6			20.97	3			20.94	2
26	20.98	6			20.94	3				
27	20.92	6			20.97	4				
28	20.93	6			20.92	4				
29	[a] 20.93	6			20.94	4				
30	[a] 20.93	6			20.97	4				
31	[a] 20.96	6			20.96	4				
32	[a] 20.93	6			20.99	4				
33	[a] 20.99	6			20.94	4				
34	[a] 20.96	6			20.92	4				
35	[a] 20.94	6			20.94	4				
36	[a] 20.93	6			20.96	4				
37	[a] 20.96	6			20.93	4				
38	[a] 20.94	6			20.95	4				
39					20.97	4				
40					20.97	4				
41					20.89	4				
42					20.91	4				
43					20.92	4				
44					20.96	4				
45					20.93	4				
46					20.96	4				
47					20.93	4				
48					20.92	4				
49					20.93	4				
50					20.93	4				
51					20.91	4				
52					20.90	4				
53					20.92	4				
Average	20.94±.02		20.94±.03		20.94±.02		20.91±.02		20.90±.03	

[a] These analyses were made by E. Carroll Creitz of this Bureau.

TABLE 2.—*Commercial oxygen absorbed in alkaline potassium pyrogallate*

Analysis	Carrier gas	Number of passages	O_2 observed	CO average	Reagent
	ml		%	%	
1	20	6	99.88		
2	20	6	99.86	a 0.03	1
3	20	6	99.86		
4	21	6	99.89		
5	21	6	99.85		
6	30	6	99.80		
7	21	6	99.79	b 0.03	2
8	21	6	99.82		
9	21	6	99.89		
10	21	6	99.81		
Average (10 analyses)			99.85±0.03		
11	59	6	99.93		
12	68	6	99.89		
13	66	6	99.88		
14	66	6	99.76	a 0.03	3
15	66	6	99.91		
16	66	6	99.85		
17	66	6	99.88		
18	61	6	99.84		
19	61	8	99.88		
20	61	8	99.84		
21	61	6	99.85	b 0.07	4
22	61	6	99.78		
23	61	6	99.86		
24	62	6	99.79		
25	62	6	99.75		
Average (15 analyses)			99.85±0.04		
Average (25 analyses)			99.85±0.04		

a Estimated.
b Measured.

TABLE 3.—*Commercial oxygen absorbed in 2.2 M chromous chloride*

Analysis	Carrier gas	Number of passages	O_2 observed	H_2 average	Reagent
	ml		%	%	
1	21	3	99.79		
2	22	4	99.87		
3	22	5	99.82		
4	21	5	99.69		
5	22	8	99.77	a 0.05	1
6	22	13	99.92		
7	22	10	99.83		
8	22	10	99.79		
9	22	10	99.89		
10	22	10	99.82		
Average (10 analyses)			99.82±0.05		
11	66	6	99.90		
12	66	6	99.81		
13	66	6	99.90		
14	66	6	99.81		
15	66	6	99.93	a 0.02	2
16	66	6	99.92		
17	66	6	99.80		
18	66	6	99.90		
19	66	6	99.82		
20	66	6	99.91		
Average (10 analyses)			99.87±0.05		
Average (20 analyses)			99.85±0.05		

a Measured.

TABLE 4.—*Commercial oxygen absorbed in 0.4 M chromous sulphate*

Analysis	Carrier gas	Number of passages	O_2 observed	H_2 average	Reagent
	ml		%	%	
1	28	12	99.45	[a] 0.11	1
2	29	12	99.61		
3	29	12	99.58		
4	20	18	99.70	[a] 0.00	2
5	20	4	99.51		
6	20	4	99.48		
7	21	6	99.91		
Average (7 analyses)			99.61±0.12		
8	68	12	99.79	[a] 0.01	3
9	68	12	99.85		
10	68	12	99.89		
11	68	12	99.87		
12	68	12	99.86		
13	66	12	99.95	[b] 0.00	4
14	66	12	99.89		
15	66	12	99.96		
16	66	12	99.88		
17	65	12	99.77	[a] 0.01	5
18	65	12	99.81		
19	65	12	99.89		
Average (12 analyses)			99.87±0.04		
Average (19 analyses)			99.77±0.14		

[a] Measured.
[b] Estimated.

These results are arranged with reference to the analyses from each portion of a given reagent, the amounts of nitrogen used as a carrier gas and the number of passages of the samples through each reagent. Since the carrier gas was stored above the reagent at the beginning of each analysis, it made one less passage through the reagent than did the sample. The volume of the sample of oxygen was approximately 80 ml for each of the analyses.

The principal sources of systematic errors in the average observed percentages of oxygen reported in tables 2, 3, and 4 are:

1. The evolution of hydrogen from the chromous solutions or of carbon monoxide from the alkaline potassium pyrogallate. (The presence of either of these gases in the gas which remained after the absorption of oxygen would be measured as nitrogen from the sample and cause the apparent percentage of oxygen to be low.)

2. The transfer of nitrogen between the reagents and the samples of gas being analyzed.

The errors from the first of these two sources were measured for 8 of the 11 portions of reagents used to obtain the data given in tables 2, 3, and 4. These measured percentage errors are given in columns 5 of these tables.

The carrier gas from analyses 1 to 3, inclusive, and 11 to 17, inclusive, of table 2 was not examined for carbon monoxide. The percentages (0.03%) marked "estimated" in column 5 of this table are based on previous experience with this combination of reagent, gas sample, and absorption pipette.

The carrier gas from analyses 13 to 16, inclusive, of table 4 was not analyzed. Because of the high average percentage of oxygen observed in these analyses, it has been assumed that the amounts of

hydrogen evolved were sufficiently small to be neglected without serious error.

When the observed percentages of oxygen which are reported in tables 2, 3, and 4 are corrected for the evolution of hydrogen or of carbon monoxide, the average corrected percentages of oxygen are as follows:

By absorption in alkaline potassium pyrogallate	99.89 ±0.04%.
By absorption in concentrated chromous chloride	99.88 ±0.05%.
By absorption in chromous sulfate	99.79 ±0.12%.

The greater part of the differences between these average corrected percentages of oxygen may be traced to incomplete re-solution of the nitrogen which has been displaced from the reagents during the first few passages of each analysis. This re-solution is effected by passing the carrier gas through the reagents during the latter part of each analysis. Therefore, the amounts of nitrogen which are dissolved in this way will depend in part on the number of passages made during the analyses and the volume of carrier gas which is used.[14]

In order to examine the effect of using large or small volumes of carrier gas, the percentages reported in tables 2, 3, and 4 have been separated into two groups according to the approximate amounts of nitrogen which were used in the analyses and the average number of times this nitrogen was passed through the reagents.[15]

The average corrected percentages of oxygen observed when approximately 20 ml of carrier gas was used are as follows:

1. By alkaline potassium pyrogallate, 6 passages	99.88 ±0.03%.
2. By chromous chloride, concentrated, 6 passages	99.87 ±0.05%.
3. By chromous sulfate, dilute, 10 passages	99.65 ±0.12%.

The average corrected percentages of oxygen observed when approximately 60 ml of carrier gas was used are as follows:

4. By alkaline potassium pyrogallate, 6 passages	99.90 ±0.04%.
5. By chromous chloride, concentrated, 6 passages	99.89 ±0.05%.
6. By chromous sulfate, dilute, 12 passages	99.87 ±0.04%.
7. By chromous chloride, concentrated, 12 passages [16]	99.91 ±0.05%.
8. By alkaline potassium pyrogallate, 12 passages [16]	99.92 ±0.04%.

The errors shown by the large differences between the average corrected percentages of oxygen reported in 1, 2, and 3 become smaller when the amounts of carrier gas are increased from 20 to 60 ml. Therefore, if the analyst is not concerned with errors which are less than approximately 0.05 percent, the discussion of these first three series of analyses may be limited to a simple warning that large volumes of carrier gas should be passed repeatedly through solutions of chromous sulfate when this reagent is used to determine oxygen volumetrically.

If, however, the analyst is concerned with errors of approximately 0.01 or 0.02 percent, the differences between the average corrected percentages reported in 4, 5, 6, 7, and 8 are significant.

[14] The amounts of "carrier" or "push" gas used in volumetric gas analysis vary considerably. Many analysts use none whatever, and amounts of less than 20 ml are used more frequently than larger volumes.

[15] It should be noted that any oxygen which does not react during the earlier analyses of a series will remain in the carrier gas and have the opportunity to react during the analyses which follow. Therefore, only that oxygen, if any, which does not react in the last analysis of a series will affect the average percentage of oxygen calculated from the series of analyses. The possibility of incomplete absorption of oxygen measurably affecting the average results of a series of analyses is, therefore, extremely remote.

[16] These data are not given in tables 2 and 3. They were obtained by making additional passages of nitrogen in analyses 11 to 20, inclusive, of table 3 and 18 to 25, inclusive, of table 2.

The discussion of the possible sources of error which are indicated by the differences between these average corrected percentages is made difficult by the fact that the actual percentage of oxygen in the samples which were analyzed is not known. Furthermore, since the errors from all sources are measured simultaneously it is not possible to arrive at a definite conclusion regarding the magnitude of the error from a single source.

One source of probable error in these results is the change of solubility of nitrogen in the reagents with the changes of temperature which are caused by the heat liberated when oxygen reacts with them. The changes of solubility of nitrogen in 220 ml of chromous sulfate, chromous chloride, and alkaline pyrogallate are reported in section VII as 0.025, 0.01, and 0.003 ml/°C, respectively.

The effect of change of temperature during a series of analyses depends on the temperature of the reagent at the start of the first analysis and at the end of the last analysis of the series.

The changes of temperature which occurred during many of the analyses reported in tables 2, 3, and 4 were not recorded. The increase of temperature, after 12 passages of carrier gas, during analyses 11 to 20, inclusive, of table 3 was 4.1° C, or approximately 0.4° C for each analysis, while the increase during analyses 17 to 19, inclusive, of table 4 was 2.2° C, or 0.7° for each analysis.[17]

These changes of temperature, together with the temperature solubility coefficients of nitrogen given above, correspond to a correction of about 0.02 percent in the average percentage of oxygen as determined by absorption in chromous sulfate and about 0.01 percent when the absorption was made by 12 passages through chromous chloride. The corresponding estimated change in the average percentage of oxygen as determined by 12 passages through alkaline potassium pyrogallate is negligibly small.

When the percentages given in 6, 7, and 8 of page 58 are corrected for changes of solubility of nitrogen in the reagents with temperature they become:

9. By chromous sulfate ..... $99.89 \pm 0.04\%$.
10. By chromous chloride, concentrated ..... $99.92 \pm 0.05\%$.
11. By alkaline potassium pyrogallate ..... $99.92 \pm 0.04\%$.

Two additional possible sources of error in these corrected results will be discussed briefly. The first of these is the possibility that the reagents were not saturated with nitrogen at the final temperature of the reagents when 60 ml of nitrogen was passed through them 12 times during each analysis.

On the basis of the data reported in RP1113, it appears that these reagents were substantially saturated with nitrogen (± 0.02 ml) after six passages of 60-ml portions of carrier gas had been made. Therefore, it is concluded that no measurable error caused by failure to saturate the reagents with nitrogen is involved when the sample and 60 ml of carrier gas were passed 12 times through the reagents.

A second possible source of error in these corrected results is indicated by the measurements reported in RP1113. This paper shows that measurable volumes of nitrogen may pass through the open surface of these reagents in the atmospheric arm of the absorption

[17] When a series of analyses is made in rapid succession, the temperature gradient which develops between the reagents and the air of the laboratory cools the reagents much more rapidly than when only a single analysis is made.

pipettes and that a layer of liquid petrolatum over the alkaline potassium pyrogallate will not prevent this passage. The direction and rate of this passage of nitrogen depend on the fractional saturation of the surface of the reagents with nitrogen as compared to the partial pressure of nitrogen in the gas above the open surface of the reagent. The rate of passage is also proportional to the solubility of nitrogen in the reagent.

On the basis of the amounts of dissolved nitrogen which are displaced from the solutions of chromous sulfate and chromous chloride during the absorption of oxygen (see section VII), and the solubility of nitrogen in chromous sulfate, chromous chloride, and alkaline potassium pyrogallate (see RP1113), much more nitrogen may dissolve through the open surface of chromous sulfate than of chromous chloride, while very small amounts of dissolved nitrogen may pass from the potassium pyrogallate into the air above the oil on its open surface. In addition to the loss of dissolved nitrogen from potassium pyrogallate, very small bubbles of this gas have been observed to pass from the distributor tip and through the open surface in the atmospheric arm of the absorption pipette during analyses. This occurs when the rate of passage of gas into the pipette from the burette is so rapid that the very small bubbles are carried downward with the displaced liquid into the atmospheric arm of the pipette. The amounts of nitrogen lost from the burette in this way may be as much as 0.001 ml per passage. A similar loss of gaseous nitrogen through the chromous solutions is thought not to have occurred.

It is not possible to estimate the effect of the passage of nitrogen through the open surface of the reagent on the percentages reported in 9, 10, and 11. It is quite possible, however, that the passage of dissolved nitrogen may have been responsible for the greater part of the difference between these final percentages.

IX. CONCLUSION

The agreement which may be obtained between the average corrected percentages of oxygen as determined by absorption in these reagents is of interest. From a practical standpoint, however, the analyst is concerned with observed rather than with corrected results. On this basis, alkaline potassium pyrogallate or concentrated solutions of chromous chloride are to be preferred to dilute solutions of chromous sulfate when mixtures of oxygen and nitrogen are to be analyzed.

Many other secondary factors should be considered when the choice of an oxygen absorbent is to be made. Some of these will be discussed briefly.

Alkaline potassium pyrogallate may be prepared somewhat more rapidly than either of the chromous solutions, provided a stock solution of the proper concentration of potassium hydroxide is available. On the other hand, if the need of concentrated chromous chloride is anticipated it may be prepared and kept over amalgamated zinc in a loosely stoppered flask. This reagent must, however, be saturated with nitrogen and freed from dissolved hydrogen before being used.

The volume of oxygen which may be completely absorbed by alkaline potassium pyrogallate has been reported [18] as about 27 times the volume of the reagent when the absorption is made by shaking the

[18] See footnote 7, page 49.

sample in a Hempel pipette over mercury. This capacity, however, was not realized in the analyses reported in this paper because the small perforations in the distributor tips of the absorption pipettes became clogged with a precipitate after the volume of absorbed oxygen approached three time the volume of reagent. The volume of oxygen which may be absorbed in chromous chloride will vary with the concentration of the solution. One volume of a 2 *M* solution of chromous chloride will absorb about eight volumes of oxygen before the concentration of bivalent chromium decreases to 0.5 *M*. The time required to absorb the oxygen from a given sample and to redissolve most of the nitrogen which has been displaced from the reagent is less when either potassium pyrogallate or concentrated chromous chloride is used than with dilute chromous sulfate.

The passage of the samples through the chromous solutions does not give rise to foaming. When alkaline potassium pyrogallate is used, foaming may occur and cause delay before the gas can be returned to the burette for measurement.

The passage of very small bubbles of gas from the sample and the loss of these bubbles in the atmospheric arm of the absorption pipette, which occurs when the samples are passed rapidly through alkaline potassium pyrogallate, do not occur when the chromous solutions are used in the same type of absorption pipette.

The chromous solutions do not etch stopcocks rapidly, if at all.

When the samples to be analyzed contain gases other than oxygen and nitrogen, the solution and displacement of each of the "inert" constituents of the samples in the oxygen-absorbent must be considered carefully. Nitrogen is less soluble in alkaline potassium pyrogallate than in either of the chromous solutions, but little is known concerning the solubility of other inert gases in these reagents. Therefore, until data concerning these solubilities are available it is unwise to change from a reagent which has been used over long periods to one with which the analyst is unfamiliar.

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DISPLACEMENT OF NITROGEN FROM AND ITS SOLUTION IN CERTAIN REAGENTS DURING VOLUMETRIC GAS ANALYSIS

By Joseph R. Branham and Max Sucher

ABSTRACT

This paper deals with errors in volumetric gas analysis caused by the displacement of nitrogen from and its solution in liquid reagents when these are used to remove a reactive gas from a gas mixture. The data show that measurable volumes of nitrogen may be exchanged between the gas sample and the reagent, as well as between the atmosphere and the reagent at the surface of separation in the atmospheric arm of the absorption pipette. Volumetric errors may also result from the change of solubility of nitrogen in the reagent with temperature when heat is liberated during the absorption of a reactive gas. Errors from these sources are roughly proportional to the solubility of nitrogen in the reagents.

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I. INTRODUCTION

In volumetric gas analysis the apparent percentage of each reactive constituent of the sample of gas being analyzed is obtained from the change of volume which occurs when the reactive constituent is removed. This removal is accomplished chemically by passing the sample over or through, or shaking it with, appropriate liquid reagents. It is customary to saturate these reagents before the analysis with the inert gas of the sample and thereby fix the dissolved inert at an amount which can be reproduced during subsequent operations. Since the partial pressure of the inert gas in the sample is less than

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atmospheric, some of the gas dissolved in the reagent will be displaced during the passages which are required for the removal of the reactive constituent. Since the continued presence of this displaced gas in the gas phase would result in a low apparent percentage of the reactive constituent, the displaced gas is redissolved wholly or in part by repeated passages of the gas which remains after the chemistry of the analysis has been completed.

In the course of a series of experiments which were made to determine the suitability of chromous solutions [1] as reagents for oxygen in gas analysis, the accuracy of the results was found to be affected by the displacement of nitrogen [2] from, and its subsequent partial re-solution in, the reagents. The present study was undertaken to find out why nitrogen was more readily transferred between the chromous solutions and the gas being analyzed than between potassium pyrogallate and samples of gas under similar conditions.

The data which are reported in this paper were obtained by measuring (1) the oxygen which was displaced, and (2) the nitrogen which dissolved when nitrogen was bubbled through several solutions which had previously been saturated with air. The first of these measurements is of the same nature as the displacement of nitrogen from a reagent during the chemical absorption of oxygen, while the second corresponds to the re-solution of any nitrogen which was displaced during the first few passages of the gas through the reagent.

II. PREPARATION AND CHOICE OF SOLUTIONS

Since the solutions were saturated with air at the start of the experiments, those which react chemically with oxygen could not be used to obtain the data desired. For this reason solutions of chromic chloride, chromic potassium sulfate, and potassium hydroxide were examined on the assumption that nitrogen would be transferred in them in a manner similar to its transfer in solutions of chromous chloride, chromous sulfate, and alkaline potassium pyrogallate. Air-saturated distilled water was also used to furnish a basis for comparison.

The solutions examined were:

1. A 4 *M* solution of green chromic chloride to which was added 10 percent by volume of concentrated hydrochloric acid. (The solutions of chromous chloride reported in RP1112 were prepared by reducing this mixture with amalgamated zinc.)

2. A 0.4 *M* solution of chromic potassium sulfate. (The solutions of chromous sulfate reported in RP1112 were prepared by reducing a solution of this concentration with amalgamated zinc.)

3. A solution prepared by adding 10 ml of water to 100 ml of a solution of potassium hydroxide with a specific gravity of 1.54 at 20° C. (The concentration of potassium hydroxide in this solution is approximately the same as that used to prepare alkaline potassium pyrogallate in this laboratory.)[3] This solution of potassium hydroxide is approximately 12 *N*.

4. A 3 *N* solution of potassium hydroxide. (This solution, which contains about 15 percent by weight of KOH, was selected after the

[1] J. R. Branham, *Preparation and application of chromous solutions for the absorption of oxygen in volumetric gas analysis.* J. Research NBS **21**, 45 (1938) RP1112.

[2] The term "nitrogen" is used throughout this paper to include the normal constituents of air after the removal of oxygen and carbon dioxide.

[3] These solutions are prepared in the manner recommended by R. P. Anderson, J. Ind. Eng. Chem. 7, 578 (1915).

more concentrated solutions of potassium hydroxide had been examined, in order to obtain additional data regarding the solubility and transfer of nitrogen.)

5. Distilled water.

All of these liquids were saturated by bubbling air freed from carbon dioxide through them before they were transferred to the absorption pipettes attached to the volumetric apparatus.

III. APPARATUS

The volumetric measurements were made over mercury in an apparatus previously described.[4] The reproducibility of measurement of a fixed volume of gas in this apparatus is ± 0.02 ml. Each determination of the nitrogen which dissolved or the oxygen which was displaced depended on two volumetric measurements. When solutions of chromic chloride were examined three measurements were required because of the presence of carbon dioxide (see section IV). Errors of volumetric measurement are carried forward during the examination of each solution and become more significant the less the solubility of nitrogen. The mesaured volumes of gas were reduced to 0° C and to a pressure of 760 mm of Hg before being plotted.

The air-saturated solutions were examined in two Schott & Genossen absorption pipettes. These are equipped with fritted-glass distributor tips of "porosity G2."[5] The oxygen displaced from the various solutions was determined by absorption in alkaline potassium pyrogallate.

IV. EXPERIMENTAL PROCEDURE

The following procedure was employed to measure the volumes of nitrogen and oxygen transferred between the various air-saturated solutions and the nitrogen which was bubbled through them.

1. Approximately 220 ml of one of the air-saturated solutions was put into each of two absorption pipettes.

2. The volumetric apparatus, including the capillary connections above the solution in the pipettes, was filled with nitrogen. The open surface of the liquid in one pipette was in contact with an atmosphere of air (fig. 1, case 1).

3. An atmosphere of nitrogen (or an oil seal) was imposed above the open surface in the other pipette (fig. 1, case 2).

4. Approximately 60 ml of nitrogen was measured in the burette and passed 10 times through the solution in one of the two pipettes. (When nitrogen was passed through the water, 5, instead of 10, passages were made initially.)

5. The gas which had lost some nitrogen to the solution and had gained some oxygen from it was brought back into the burette and measured.

6. The volume of oxygen gained was determined by absorption in potassium pyrogallate. The residue which now remained was a measured quantity of nitrogen which was immediately used to repeat the procedure with the solution in the second pipette, beginning with step 4.

The volume of nitrogen which dissolved in the liquids during the passages of step 4 in each case was calculated by subtracting the

[4] Martin Shepherd, BS J. Research **6**, 121 (1931) RP266.
[5] These are listed as 153–SG2 in catalog of Fish-Schurman Corporation, New York City.

volume after step 6 from the volume at the beginning of step 4. Since the measurements were made alternately under the conditions of case 1 and case 2, the observed volume after step 6 of case 1 (or case 2) becomes automatically the initial volume of step 4 in the other case which followed.

In the calculations, this quantity is the subtrahend in one case and the minuend in the case immediately following. For this reason an error of measurement at this point affects the calculated volume of dissolved nitrogen equally but in opposite directions in any two successive determinations. The errors of this particular measurement

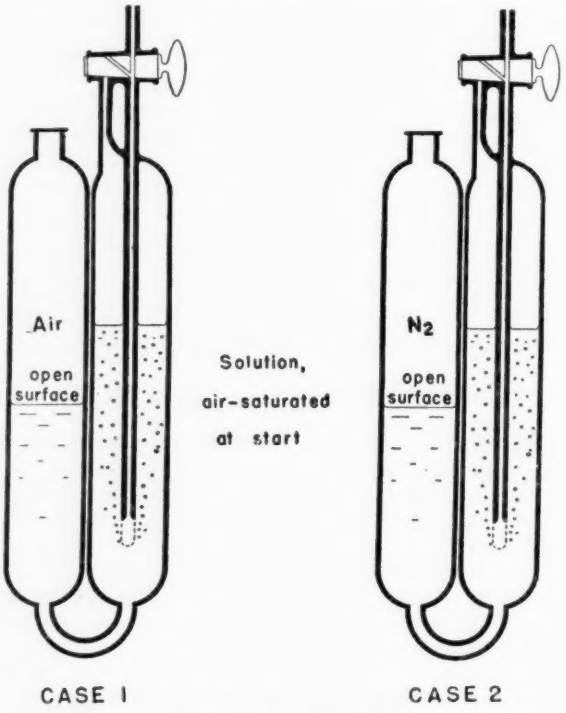

FIGURE 1.—*Absorption pipettes in cases 1 and 2.*

will, therefore, affect the series of data for each case, taken separately, but cancel if the data for the two cases are averaged.

The procedure, with each of the liquids examined, was repeated at fairly regular intervals except during the overnight recess. About 24 hours elapsed between the first and seventieth passages in each set of experiments.

When nitrogen was passed through a saturated solution of green chromic chloride, which had previously been acidified with hydrochloric acid and had had carbon dioxide-free air bubbled through it for 18 hours, carbon dioxide was found in the emergent nitrogen. The volumes of carbon dioxide were readily measurable, ranging up to 0.2 ml, and were roughly proportional to the time which elapsed between two series of passages of nitrogen through the acidified

solution. The identification of the gas was made by passing carbon dioxide-free air through the acidified solution and then through solutions of calcium hydroxide and lead acetate. The calcium and lead salts which precipitated were examined microscopically [6] and identified as $CaCO_3$ and $PbCO_3$. The nearly constant rate of evolution of carbon dioxide from the acidified solutions containing chromic chloride suggests the presence of carbonate combined with chromium in a manner similar to the relation which exists between part of the chlorine in green chromic chloride and the chromium in that molecule.[7]

When this solution was used to obtain the data given in figure 4 (C) it was necessary to remove the carbon dioxide which was displaced from it before the oxygen could be determined.[8] This was done by passing the gas containing carbon dioxide through a 12 *N* solution of KOH. This extra step in the procedure may have been responsible for some of the irregularities observed in the data given in figure 4 (C).

V. DISPLACEMENT OF OXYGEN AND THE SOLUTION OF NITROGEN IN WATER AND IN SEVERAL AQUEOUS SOLUTIONS

The data given in figures 2, 3, and 4 resulted from the series of operations described in section IV. The open surface of one portion of liquid in the atmospheric arm of absorption pipette *A* was in direct contact with air (case 1, fig. 1), while the open surface of the second portion was in pipette *B* in direct contact with an atmosphere of nitrogen (case 2, fig. 1).[9]

The open circles represent the volumes of oxygen which were displaced in case 1, the closed circles are the volumes of oxygen displaced in case 2. The open triangles are the volumes of nitrogen which were dissolved in case 1 and the closed triangles those which dissolved in case 2. The observed volumes have been multiplied by correction factors, which vary from 0.87 to 0.89, to reduce them to 0° C, 760-mm pressure. Theoretically, the uncorrected data may be more directly comparable than the corrected data, but since the difference between the correction factors is small there is some advantage in correcting to standard conditions.

The upper horizontal broken line in figure 2 is the volume of oxygen, at 0° C, 760-mm pressure, calculated as present in 220 ml of water saturated with air at the atmospheric pressure and temperature which prevailed when the data in figure 2 were secured. Similarly, the lower horizontal broken line in figure 2 is the volume of nitrogen reduced to standard conditions calculated as the difference between the nitrogen in 220 ml of air-saturated water and of nitrogen-saturated water. These values were calculated by Henry's law from the solubilities [10]

[6] This work was done by Charles P. Saylor of this laboratory.

[7] J. Olie, Jr., investigated the equilibrium between the green and violet chromic chlorides. He found that only one of the three chlorine atoms in freshly prepared green chromic chloride could be precipitated by silver nitrate. If, however, the solution was aged before adding the silver nitrate, the percentage of chlorine which reacted increased with the age of the solution. Z. anorg. Chem. **29**, 51 (1906).

[8] Anderson and Riffe have reported that a solution of chromous chloride prepared by reducing violet chromic chloride by a current of hydrogen at 400 to 500° C, absorbs oxygen rapidly but not completely. The completeness of the absorption was measured by passing the residual gas, after treatment in $CrCl_2$, through alkaline potassium pyrogallate. It is not known whether the chromous solution prepared by these authors evolved carbon dioxide, but if so, the apparent incomplete absorption of oxygen would be explained. J. Ind. Eng. Chem. **8**, 24 (1916).

[9] This atmosphere of nitrogen was maintained by connecting the atmospheric arm of pipette *B* to the burette arm of an extra pipette which contained alkaline potassium pyrogallate. The connections consisted of a rubber stopper, glass tubing and a butted glass joint covered with rubber tubing.

[10] Winkler, Ber. deut. Chem. Ges. **24**, 3606 (1891); Int. Crit. Tables. **3**, 258 (1928).

of oxygen and of nitrogen in water which is in equilibrium with a large surface of gas. Data calculated in this manner may differ from those reported in this paper, which were obtained by passing bubbles of gas through liquids. The broken curves in these figures are drawn through points midway between the volumes of oxygen displaced in case 1 and in case 2, and also midway between the volumes of nitrogen which dissolved in case 1 and in case 2. These points through which the broken curves are drawn will be referred to as average data. These data are used to calculate the curves given in figures 6 and 7.

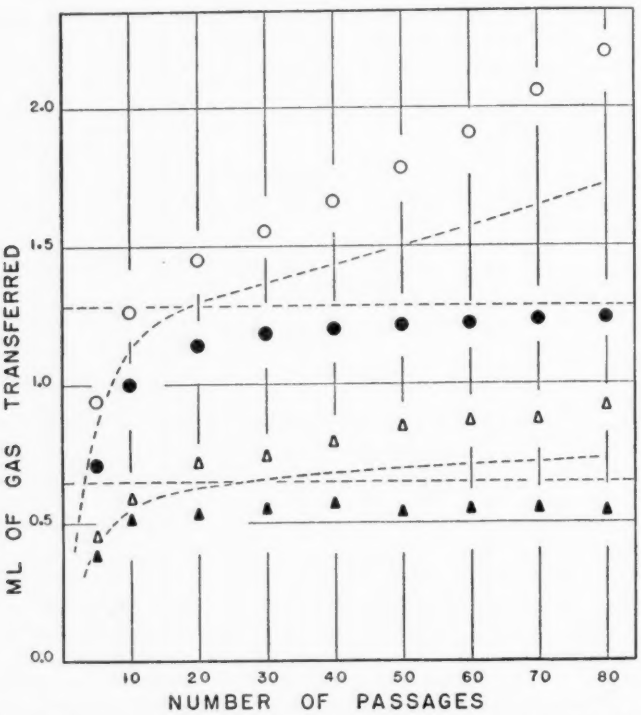

FIGURE 2.—*Volumes of oxygen and nitrogen transferred between 220 ml of water, originally air-saturated.*

The nitrogen bubbled through it as measured in the burette, corrected to 0° C, 760-mm pressure. Open circles represent oxygen liberated in case 1; filled circles, oxygen liberated in case 2; open triangles, nitrogen dissolved, case 1; filled triangles, nitrogen dissolved, case 2.

VI. TRANSFER OF GAS THROUGH THE OPEN SURFACE OF WATER AND OF SEVERAL SOLUTIONS IN ABSORPTION PIPETTES

It is evident from figures 2, 3, and 4 that the nature of the atmosphere in contact with the open surface of air-saturated liquids has a marked effect on the data obtained when nitrogen is bubbled through them. When air is above the open surface (case 1, fig. 1) and oxygen is displaced from each liquid by the passage of nitrogen through it, some oxygen from the imposed atmosphere will dissolve in the liquid through its open surface, and subsequently be displaced and measured

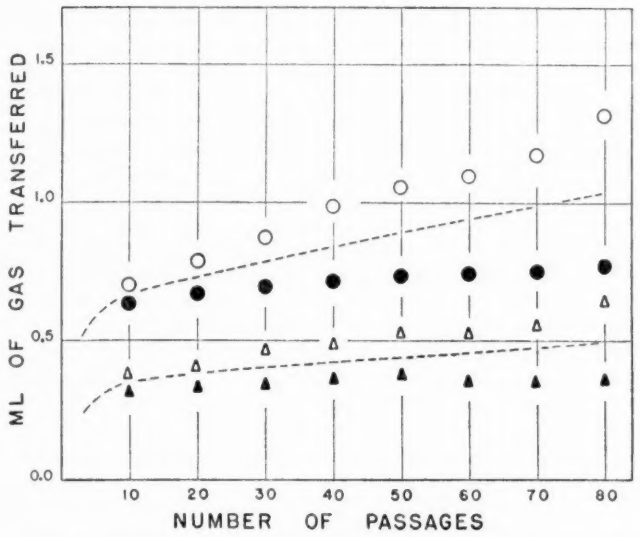

FIGURE 3.—*Volumes of oxygen and nitrogen transferred between 220 ml of 0.4 M* $K_2Cr_2(SO_4)_4$ *originally air-saturated.*

The nitrogen bubbled through it as measured in the burette, corrected to 0° C, 760-mm pressure. Symbols as in figure 2.

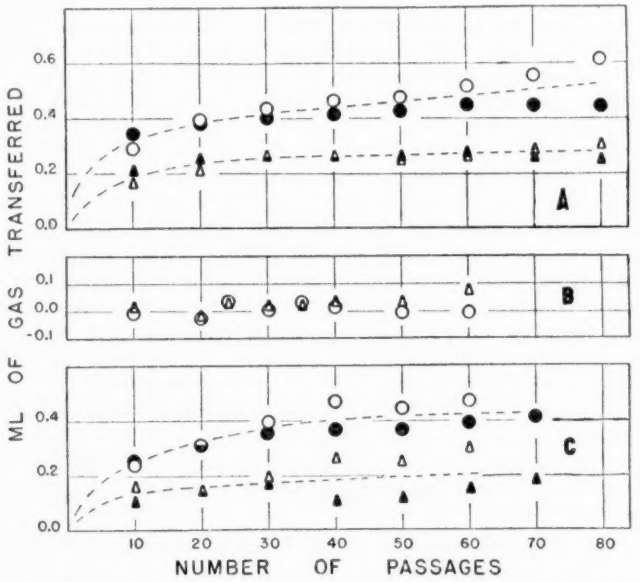

FIGURE 4.—*Volumes of oxygen and nitrogen transferred between 220 ml of (A) 3 N* KOH, *(B) 12 N* KOH, *(C) 4 M* $CrCl_3$ *+ 10 percent of* HCl *by volume.*

The solutions were initially saturated with air and the nitrogen bubbled through them, as measured in the burette, was corrected to 0° C, 760-mm pressure. Symbols as in figure 2.

in the burette, together with the oxygen in the liquid at the start of the experiment. At the same time some of the nitrogen originally in the burette will dissolve in the liquid and, subsequently as the liquid approaches equilibrium with nitrogen, will escape continuously to the air above the open surface. The measured volumes of oxygen and nitrogen transferred between the liquid and the bubbles of nitrogen under this condition (case 1) will both be greater than if no gas had passed through the open surface.

When an atmosphere of nitrogen is above the open surface of the liquid (case 2), which was originally saturated with air, nitrogen will pass continuously through the open surface and dissolve in the liquid until it has become saturated with nitrogen from this source and from the bubbles of nitrogen which originate in the burette. The nitrogen which dissolves through the open surface will evidently prevent a like amount of the nitrogen in the burette from going into solution.[11] At the same time that nitrogen is dissolving through the open surface, some of the oxygen which was dissolved in the air-saturated liquid will pass through the open surface into the atmosphere of nitrogen above it. The measured volumes of nitrogen and oxygen transferred in case 2 will both be smaller than if no gas had passed through the open surface.

The differences between each pair of oxygen curves shown in figures 2, 3, and 4 represent the oxygen which dissolved through the open surface of each liquid from the atmosphere of air (case 1) plus that which escaped from the liquid into the atmosphere of nitrogen above its open surface (case 2). Similarly, the differences between the nitrogen curves in these figures is the sum of the nitrogen which escaped through the open surface in case 1 plus that which entered the solution through this surface in case 2.

The difference between the two oxygen curves and between the two nitrogen curves in figures 2, 3, and 4 is greatest for water and becomes successively smaller with 0.4 *M* $K_2Cr_2(SO_4)_4$, 3 *N* KOH, and 4 *M* $CrCl_3$ + HCl, in that order. When the 12 *N* solution of KOH was examined under case 1 the amounts of oxygen and of nitrogen which were exchanged between this solution and the nitrogen bubbled through it were of the same order of magnitude as the precision of a single measurement made with the volumetric apparatus. For this reason only one oxygen and one nitrogen curve were obtained. The difference between these data and those which might have been secured in case 2 will evidently be too small to measure with the volumetric apparatus employed.

Further discussion of these data is given in section IX.

VII. APPROXIMATE SOLUBILITIES OF NITROGEN AND OF OXYGEN IN THE SOLUTIONS EXAMINED

The data of figures 2, 3, and 4 will be used to determine the approximate solubilities of oxygen and of nitrogen in the liquids examined in this work. These data must be considered from two standpoints; (1) The number of passages of nitrogen through the liquids required

[11] Effects of this kind are to be expected to some extent whenever an atmosphere of nitrogen is above the open surface of a reagent which is only partially saturated with nitrogen. This source of error in volumetric gas analysis has been mentioned in paragraph 4 of the introduction and is discussed in section XII.

to establish equilibrium and (2) the ordinate values corresponding to the number of passages chosen as indicative of equilibrium.

The passage of oxygen and nitrogen through the open surface of the liquids in the atmospheric arm of the absorption pipettes prevents the establishment of equilibrium under the conditions of case 1. The number of passages of nitrogen required to equilibrate the liquids with nitrogen must, therefore, be based on the data obtained under the conditions of case 2.

The shapes of the curves located by the position of the solid triangles in figures 2, 3, and 4 indicate that each of the liquids was substantially saturated with nitrogen during the first 30 passages of nitrogen through them. This indication is substantiated to some extent by the fact that the curve of the average data (fig. 2) and the horizontal line determined from saturation data intersect at about this abscissa.

The curves determined by the solid circles continue slightly upward beyond abscissa 30, about 0.05 ml of oxygen apparently being displaced from each of the liquids except 12 *N* KOH between the thirtieth and seventieth passages of nitrogen. Experiments made by confining atmospheric nitrogen in the volumetric apparatus and by passing the confined nitrogen through potassium pyrogallate after the nitrogen had been in the apparatus for several days showed that small amounts of oxygen had diffused into the apparatus. The rate of diffusion of oxygen into the apparatus was about 0.03 ml each 24 hours. It is probable that this oxygen entered the volumetric apparatus through the short rubber connections which covered the butted glass joints between the various units which make up the volumetric apparatus. In view of this fact it is probable that no significant volumes of oxygen were displaced from the liquids by the passage of nitrogen through them after 30 passages had been made in the first few hours of experiments. However, since this is not certain, the data will be examined on the assumption that the liquids were in substantial equilibrium with nitrogen and contained no significant amounts of oxygen after the number of passages of nitrogen through them was somewhere between 30 and 50.

As was shown in section VI, the amounts of nitrogen which had apparently dissolved in each of the liquids and the amounts of oxygen which were displaced from them are greater in case 1 and less in case 2 than they would have been if no gas had passed through the open surfaces in the atmospheric arm of the absorption pipettes. The solid triangles and circles between the thirtieth and fiftieth abscissas of figures 2, 3, and 4, therefore, lie below the ordinate values which would have been obtained at equilibrium if no gas had passed through the open surfaces. Similarly, the open circles and triangles lie above the ordinate values sought.

For convenience the average value of these two ordinates at 30 passages and the corresponding average at 50 passages were used to denote the approximate solubility of nitrogen and oxygen given in table 1.

TABLE 1.—*Average volume of nitrogen or oxygen transferred to or from 220 ml of air-saturated solutions when nitrogen is bubbled through them until saturated*

1	2	3	4	5	6	7	8	9
Liquid	Avg ml of N_2	Avg ml of O_2	N_2 ratio	O_2 ratio	Avg ml of N_2	Avg ml of O_2	N_2 ratio	O_2 ratio
	30 passages				50 passages			
Water	0.66	1.36	1.0	1.0	0.69	1.49	1.0	1.0
0.4 *M* $K_2Cr_2(SO_4)_4$	.41	.79	1.6	1.7	.43	.89	1.6	1.7
3 *N* KOH	.26	.42	2.5	3.2	.26	.46	2.6	3.3
4 *M* $CrCl_3$+10 percent of HCl	.18	.37	3.7	3.7	.19	.42	3.6	3.6
12 *N* KOH	.03?	.00?	20?	20?	.03?	.00?	20?	20?

The ratios of the volume of nitrogen which dissolved in water to the volumes of nitrogen which dissolved in each of the solutions are given in columns 4 and 8. Similar ratios for the displaced oxygen are given in columns 5 and 9. It may be noted that these ratios are substantially independent of the number of passages chosen as the criterion of equilibrium. These ratios are used to calculate the data given in figures 6 and 7.

The approximate total volumes of nitrogen dissolved in 220 ml of the solutions examined when these are in equilibrium with nitrogen are given in column 2 of table 2. These values were obtained from the average of columns 2 and 6 of table 1 by multiplying by $1/(1-0.7905)$ in accordance with Henry's law. Column 3 of table 2 is included for the benefit of readers who use larger or smaller volumes of reagents in absorption pipettes.

TABLE 2.—*Approximate total volumes of nitrogen dissolved in several solutions*

	Milliliters of N_2 in 220 ml	Milliliters of N_2 in 100 ml
Water	3.2	1.5
0.4 *M* $K_2Cr_2(SO_4)_4$	2.0	.9
3 *N* KOH	1.2	.6
4 *M* $CrCl_3$+10 percent of HCl	.9	.4
12 *N* KOH (estimated) or alkaline potassium pyrogallate	.2	.1

On the basis of the assumption made in the first paragraph of section II, 220 ml of chromous sulfate, chromous chloride, and alkaline potassium pyrogallate, respectively, will contain approximately 2.0, 0.9, and 0.2 ml of dissolved nitrogen when saturated with this gas under laboratory conditions. In other words, these are the volumes of dissolved nitrogen in these reagents at the beginning of an analysis and also those which must be in solution at the end of the analysis if the analytical results are to be correct.

VIII. EFFECT OF A FLOATING OIL SEAL ON THE PASSAGE OF GAS THROUGH THE OPEN SURFACE

The data given in figure 5 were obtained from two 220-ml portions of water which were saturated with air at 23.5° C and 753-mm pressure. The open circles and triangles represent the volumes of oxygen and nitrogen which were transferred when the open surface of the

water was in direct contact with air (case 1). The closed circles and triangles represent the corresponding volumes of oxygen and nitrogen which were transferred when a 1-inch layer of liquid petrolatum floated on the open surface of the water and prevented direct contact between it and air. The horizontal broken lines have the same significance as in figure 2. The volumes of dissolved oxygen and nitrogen in the layer of liquid petrolatum are not known. Approximately 24 hours elapsed between the first and seventieth passages of nitrogen through the water in the pipettes.

The curves indicate that the oil seal does not prevent the passage of oxygen and nitrogen through the open surface of the water. The

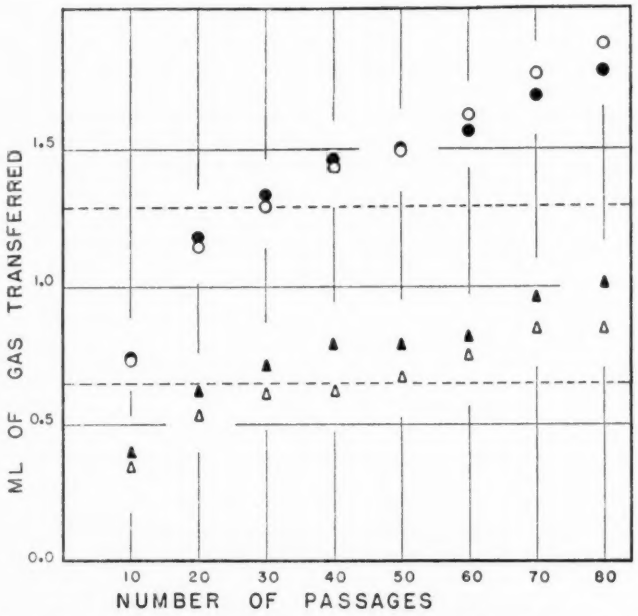

FIGURE 5.—*The volumes of oxygen and of nitrogen transferred between 220 ml of water, originally air-saturated.*

The nitrogen bubbled through it when the open surfaces were in contact with air and when covered by an oil seal.

escape of nitrogen under these conditions will prevent the establishment of an equilibrium between the water and the nitrogen which is bubbled through it and, if such an equilibrium is approached, the layer of oil will not preserve this condition for any extended period of time.

IX. EXCLUSION OF AIR ABOVE THE OPEN SURFACE BY MEANS OF A NITROGEN-FILLED RUBBER BALLOON

Data were obtained when the open surface of air-saturated water was kept under an atmosphere of nitrogen by means of a balloon which was inflated with nitrogen just before the start of the experiment. Under these conditions there was little or no difference be-

tween the rate of transfer of nitrogen in this pipette and in a pipette where an atmosphere of nitrogen was maintained by connections to an extra pipette containing potassium pyrogallate. In view of the fact that oxygen and nitrogen pass through rubber rather readily this result was surprising. There is little doubt, however, that the nitrogen-filled balloon, over the period of 3 days covered by the measurements, offered much better protection against the passage of oxygen through the atmospheric arm of a pipette than a 1-inch layer of liquid petrolatum. It does not follow, however, that as ordinarily used the rubber balloon will offer better protection than the oil seal. Balloons are usually left in place for a long time and may approach approximate equilibrium with the surrounding air instead of being filled with an atmosphere free from oxygen as at the start of this experiment.

X. DISCUSSION OF THE DATA

In figure 6 the ordinate scales of the average data obtained from each solution given in figures 2, 3, and 4 have been multiplied by the factor for that solution given in columns 4 and 5 of table 1. Simi-

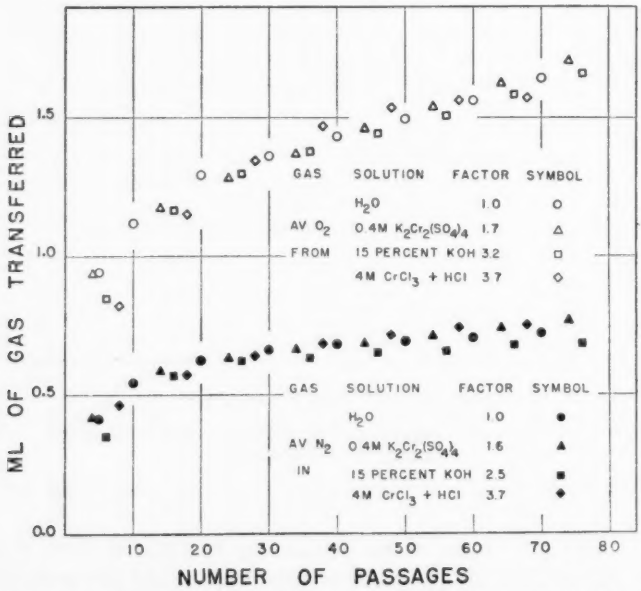

FIGURE 6.—*Data from figures 2, 3, and 4 on vertical scales multiplied by the solubility factor based on 30 passages of nitrogen.*

larly, figure 7 was obtained by multiplying these average data by the factor given in columns 8 and 9 of table 1. This treatment automatically brings the data from each solution into agreement with water at the ordinate corresponding to 30 passages of nitrogen in figure 6 and 50 passages of nitrogen in figure 7. It will not, however, secure agreement at other points unless the location of these points is proportional to the relative "solubilities" of oxygen and of nitrogen in the solutions examined. The agreement among the data in figures

6 and 7 during the first 20 passages of nitrogen through the liquids is not as close as in the remainder of the passages. It is probable that the influence of the size of the bubbles [12] of nitrogen, as well as experimental errors, may have affected these results.

Some of the conclusions to be drawn from the fairly good agreement between the data for various solutions when treated as described are of general importance in volumetric gas analyses which employ absorption methods. These may be summarized as follows.

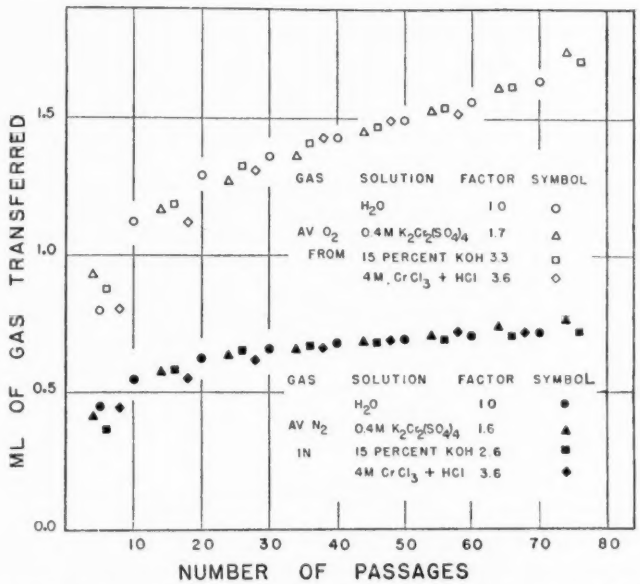

FIGURE 7.—*Data from figures 2, 3, and 4 on vertical scales multiplied by the solubility factor based on 50 passages of nitrogen.*

The solubility of nitrogen in a reagent saturated with it determines approximately: (1) The amount of this gas which passes through the open surface of the solution in the atmospheric arm of the absorption pipette under a given set of conditions; (2) the amount of nitrogen which will be displaced from the solution during the first few passages of a gas sample through it; and (3) the rate at which this displaced nitrogen may be redissolved by repeated passages of nitrogen through the solution. Similarly, the amounts of oxygen which pass from the atmosphere through the open surface of solutions with which oxygen does not react, are proportional to the solubility of oxygen in the particular reagents.

[12] Data were obtained under the conditions of case 1 with an air-saturated solution of concentrated sulfuric acid. The nitrogen bubbles in this solution were noticeably larger than those in the other solutions which were studied. During the first 50 passages of nitrogen through this solution more oxygen and nitrogen were transferred between it and the nitrogen bubbles than with 0.4 *M* $K_3Cr_3(SO_4)_4$. During the earlier passages, however, the data from the acid lay below the corresponding data from the 0.4 *M* $K_3Cr_3(SO_4)_4$. The differences of slope between these results are attributed to the smaller area of contact from a given volume of nitrogen exposed by the larger bubbles.

XI. CHANGE OF SOLUBILITY OF NITROGEN WITH TEMPERATURE IN SOLUTIONS OF ALKALINE POTASSIUM PYROGALLATE AND OF CHROMOUS SULFATE

Several experiments were made to measure directly the effects of changes of temperature on the solubility of nitrogen in alkaline potassium pyrogallate and in chromous sulfate.[13] A 220-ml portion of each of these solutions was saturated by bubbling nitrogen through it in a pipette surrounded by a water bath. Measured volumes of nitrogen were then passed through each of the solutions as the temperature of the bath was changed. The open surface above the chromous sulfate was in contact with an atmosphere of nitrogen (case 2, fig. 1). The open surface of the alkaline potassium pyrogallate was protected from direct contact with air by a layer of liquid petrolatum.

The volume of nitrogen which dissolved in the alkaline potassium pyrogallate when its temperature was lowered by 23.7° C.[14] was measured as 0.06 ml, or about 0.003 ml/° C. Because of the small amount of gas which dissolved, the accuracy of this measurement is poor and the result should be regarded as an approximation. The volume of nitrogen which was displaced when the temperature of 220 ml of a nitrogen-saturated solution of chromous sulfate was increased by 10.8° C was 0.29 ml. When the temperature of this solution was then quickly lowered by 15.3° C, 0.34 ml of nitrogen dissolved in it. The average change of solubility of nitrogen in this solution was approximately 0.025 ml/° C.

XII. CONCLUSION

It has long been known that the analysis of gaseous mixtures by absorption in liquid reagents is subject to errors caused by physical solution and displacement of components of a gas mixture which themselves do not react chemically with the reagents. This paper reports experiments which illustrate the mechanics of the transfer of inert components between the samples of gas and the reagents. It is shown that when a mixture containing a reactive and an inert gas is passed through a liquid reagent which is saturated with the inert gas, the following things occur.

1. During the removal of the reactive gas in the first or the first few passages of the sample through the reagent measurable amounts of inert gas are displaced from solution.

2. The temperature of the reagent is raised by the heat of reaction with the reactive gas.

3. Because of conditions 1 and 2 the reagent now contains less inert and the gas phase more inert than at the start of the analysis.

4. If the temperature is lowered to the initial value and repeated passages of the gas made after the reaction is completed the reagent will again become saturated as at the beginning of the absorption. This requires much more time than is usually accorded in practice.

5. But even if condition 4 is reached the gas mixture which remains may not contain exactly the same amount of inert as was in the sample

[13] This solution was prepared by passing a 0.4 *M* solution of $K_3Cr_3(SO_4)_4$ over amalgamated zinc in a Jones reductor.

[14] Temperatures were measured by a thermometer immersed below the open surface of these solutions.

initially because of the passage of inert gas through the open surface of the reagent in the atmospheric arm of the absorption pipette during the analysis. The direction of this passage will depend upon the partial pressure of the inert gas in the atmospheric arm of the absorption pipette. The rate of passage is not materially changed by a 1-inch layer of liquid petrolatum floating on this surface of the reagent.

The magnitude of the error likely to occur under otherwise similar conditions is approximately proportional to the solubility of the inert gas in the reagent used, and when there is a choice of reagents this solubility should be considered. The magnitude of the error also depends upon many other variables, including the rate of absorption of the reactive gas, the composition of the reagent, the composition of the gas mixture, the form of apparatus employed, and the operating procedure. The data are not sufficiently complete to set up a general set of corrections for analyses performed under varying conditions but have been used to explain, within reasonable limits, the previously observed behavior of chromous solutions when these were used to absorb oxygen as reported in RP1112.

Fortunately, such commonly used reagents as potassium hydroxide and alkaline potassium pyrogallate will absorb but little nitrogen if the concentration of the alkali is sufficiently great. The concentration of potasssium hydroxide in both of these reagents should, therefore, be kept as high as laboratory conditions permit.

WASHINGTON, April 4, 1938.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1114

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HYDROGEN-REDUCTION METHOD FOR THE DETERMINATION OF OXYGEN IN STEEL

By John G. Thompson and Vernon C. F. Holm

ABSTRACT

A modified hydrogen-reduction method yielded accurate values for the total oxygen content of several plain carbon steels, including steels that contained small amounts of alumina and silica, but yielded low results when larger amounts of alumina were present. The method was not applicable to the determination of the oxygen content of open-hearth iron because of inability to separate surface and body oxygen in this material.

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I. INTRODUCTION

The determination of oxygen in iron and steel and its significance to manufacturers and users of these materials have been matters of interest to metallurgists for many years. A variety of analytical methods have been developed, but the relative merits and accuracy of many of the methods are still controversial questions. The report [1] of results obtained in the recent cooperative study of methods for the determination of oxygen in steel, sponsored jointly by the National Bureau of Standards and the American Institute of Mining and Metallurgical Engineers, emphasizes the difficulty of obtaining concordant results by different methods and, in many cases, by different operators using the same method. It is evident that further attention must be devoted to this problem both in perfecting the various methods and in studying their limitations before complete reliance may be attached to determinations by any one method.

One of the methods that appears promising is a modified form of the hydrogen-reduction (Ledebur) procedure. In the original Ledebur method the sample was exposed to the action of hydrogen at temperatures above 900° C; the amount of water vapor recovered from the exit gases was used as a measure of the amount of oxides reduced by the hydrogen and hence of the amount of oxygen in the steel. It was found that low recoveries of oxygen were obtained by this procedure because the carbon of the iron or steel samples enters into the

[1] J. G. Thompson, H. C. Vacher, and H. A. Bright, Trans. Am. Inst. Mining Met. Engrs. **125**, 246 (1937); J. Research NBS **18**, 259 (1937) RP976.

71531—38——6

reduction reactions, and the exit gases therefore contain appreciable amounts of CO and CO_2 as well as water vapor. Procedures were devised for the determination of the oxygen combined as carbon oxides in addition to that combined as water, which materially increased the amounts of oxygen recovered from samples of iron and steel. In the early work it was believed that the use of milled samples or drillings was impracticable because of the presence of appreciable amounts of oxygen in the form of surface films. This trouble was avoided through the use of solid samples to which antimony and tin were added to form alloys that were molten at the temperature of the determination. Although this procedure eliminated the errors due to surface oxygen, it introduced another source of error because of possible reduction of the refractory boat which contained the molten sample.

In 1934 Brower, Larsen, and Shenk [2] described a modification of the Ledebur method that appears to be a decided improvement over the older procedures. The modified procedure, however, has not as yet been widely adopted; the data of the cooperative analysis [3] included only one set of determinations by this procedure. The present work was undertaken to obtain more information about the modified hydrogen-reduction procedure, particularly in regard to the reproducibility of its results in the hands of different operators and the comparison of its results with those obtained by other methods of analysis.

II. MODIFIED HYDROGEN-REDUCTION PROCEDURE

The essential features of Brower, Larsen, and Shenk's procedure are the use of a finely milled sample, the removal of surface oxygen from the millings by a preliminary heating in hydrogen at 500 to 550° C, and the use of high-frequency induction heating to maintain the sample at 1,200° C for the determination of the "body" oxygen of the millings.

The construction and operation of the apparatus illustrated in figure 1, were essentially as described by Brower, Larsen, and Shenk. Electrolytic hydrogen, from a cylinder of compressed gas, is passed through a preliminary purification train to eliminate moisture and oxygen from the gas before it comes in contact with the sample in the furnace tube. The rate of flow of hydrogen is indicated by bubbler tubes and is maintained at approximately 30 ml per minute. Back diffusion of air is prevented by sulfuric acid bubblers, at all exits. A trap containing about 2 cm of mercury prevents the development of excessive gas pressures within the apparatus.

The sample consists of approximately 20 g of fine millings placed in a perforated Invar bucket and suspended in the center of the vertical furnace tube. With purified hydrogen passing through the apparatus, the furnace tube and contents are heated to 500 to 550° C, by means of a resistance furnace, and are maintained at this temperature for 90 minutes to remove the surface film of oxides and moisture. The hydrogen leaving the furnace during this operation usually is wasted, but, if a determination of surface oxygen is desired, the exit gases may be passed through suitable absorbents to recover the water vapor formed by reduction of the oxides.

[2] T. E. Brower, B. M. Larsen, and W. E. Shenk, Trans. Am. Inst. Mining Met. Engrs. **113**, 61 (1934).
[3] See footnote 1.

After "stripping" the surface oxygen from the sample, the resistance furnace is replaced by a high-frequency induction coil, and the temperature of the sample is raised to 1,200° C and is maintained at this temperature for 90 minutes to accomplish the reduction of the "body" oxygen in the millings. The water vapor produced by the reduction reactions is absorbed by phosphorus pentoxide in a weighing tube. The stream of hydrogen is subsequently freed from sulfur compounds and passed over a nickel-thoria catalyst maintained at 260° C, whereby the carbon oxides are quantitatively converted to methane and water vapor, the latter being absorbed in phosphorus pentoxide. The sum of the gains in weight of the two phosphorus pentoxide tubes furnishes a measure of the oxygen liberated from the oxides of the steel.

The efficiency of the nickel-thoria catalyst and the absorbents is checked periodically by a run in which a weighed amount of crystal-

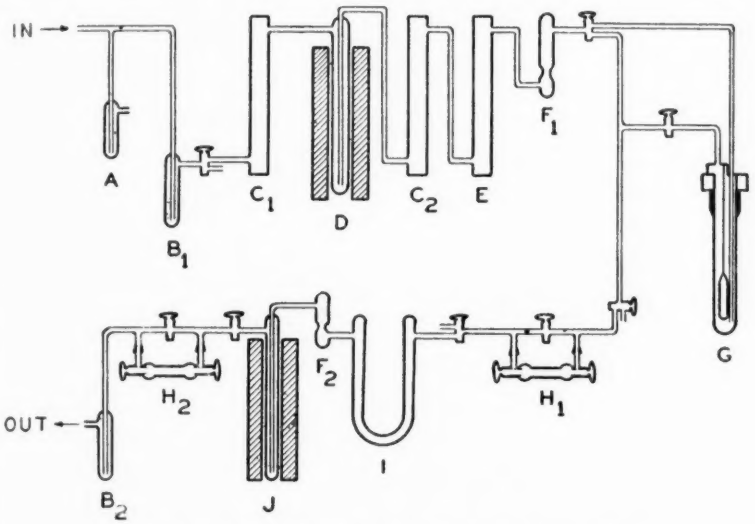

FIGURE 1.—*Sketch of the hydrogen-reduction apparatus.*

A, mercury trap; B_1, B_2, sulfuric acid bubblers C_1, C_2, soda-lime tubes; *D*, platinized silica catalyst; *E*, anhydrone tube; F_1, F_2, phosphorus pentoxide drying tubes; *G*, fused silica furnace tube; H_1, H_2, phosphorus pentoxide weighing tubes; *I*, anhydrous copper sulfate on pumice stone; *J*, nickel-thoria catalyst.

line calcite ($CaCO_3$), contained in a platinum crucible, is heated gradually to 900° C with the hydrogen flowing through the apparatus. Under these conditions the calcite is decomposed with the evolution of water vapor, carbon monoxide, and carbon dioxide which can be recovered in the analytical train in the same manner as during a determination on a sample of millings. The recovery of 95 percent or more of the theoretical amount of oxygen from the calcite indicates satisfactory performance of the apparatus.

Blank determinations on the whole apparatus, with the empty invar bucket at the operating temperature, are made periodically. The blank correction is quite constant at 0.0003 g of water for a determination of 90 minutes duration. The time required for a complete determination, including the preliminary flushing and the removal of surface oxygen, is approximately 5 hours.

III. EXPERIMENTAL

Determinations of oxygen, by the modified hydrogen-reduction procedure, were made on milled samples of seven steels and one iron. The sample material was prepared in a milling machine that was set for a depth of cut of 0.003 inch, or less. The millings thus produced were between 0.005 and 0.008 inch in thickness, according to micrometer measurements.

TABLE 1.—*Type and composition of the materials*

Number	Type of material	Composition (percent)										
		C	Si	Mn	S	P	Cr	V	Al_2O_3	SiO_2	Total oxygen	Oxygen by hydrogen-reduction (Brower and Larsen)
1	Low-carbon, rimming	0.03	0.002	0.31	0.036	0.011	0.004	<0.001	0.002	0.003	0.018	0.024
2	Medium-carbon, high-manganese, silicon-killed	.42	.26	1.15	.025	.020	.022	<.001	.002	.009	.017	.027
3	Bessemer screw stock, semi-killed	.12	.024	.72	.168	.101	.006	.004	.002	.005	.017	.027
4	Special, low-carbon, aluminum-killed	.17	.09	.65	.029	.014	.008	.001	.006	.002	.002	.008
5	Low-carbon, silicon-killed	.22	.14	.45	.042	.020	.020	.001	.002	.016	.009	.022
6	Medium-carbon, silicon-killed	.43	.20	.47	.027	.014	.012	<.001	.002	.009	.007	.010
7	Open-hearth iron, rimming	.016	.001	.024	.022	.011	.009	<.001	.002	.002	.106	.076
8	Similar to Number 4, but higher in oxygen	.20	.03	.45	.033	.014	.012	<.001	.030	.003	.017	.015

The compositions of the seven steels and one iron are shown in table 1. They were the materials used in the cooperative analysis, and the figures for Al_2O_3, SiO_2, and total oxygen are the best values derived from the results of more than two thousand analytical determinations. The Al_2O_3 and SiO_2 values were derived from the results of several different methods of analysis; the values for total oxygen were based on concordant results obtained by the vacuum-fusion method and in many cases were substantiated by results of other methods. Because of the number of analyses that were made and the variety of methods that were employed, and because the selected values are based on concordance of results obtained by several different methods, the Al_2O_3, SiO_2, and total oxygen contents of these steels can be stated with an unusual degree of certainty. The values given in table 1 are close approximations of the actual contents of Al_2O_3, SiO_2, and total oxygen, i. e., they are accurate values within the customary limits of tolerance of such determinations and are more reliable than determinations by a single operator or by a single method. The last column in table 1 lists the results reported by Brower and Larsen, in the cooperative analysis, for determinations by the modified hydrogen-reduction procedure.

The values obtained in the present study of the hydrogen-reduction method are shown in table 2, together with results of determinations by the vacuum-fusion method. The latter were made to compare results on the current samples with those previously obtained on other samples of the same material, and to provide a means for direct

comparison of results by the vacuum-fusion and hydrogen-reduction procedures when all determinations were made by the same analyst. The apparatus and procedure employed for the vacuum-fusion determinations differ from those described by Vacher and Jordan [4] in two respects (a) the two-stage mercury diffusion pump that evacuates the furnace has been replaced by a four-stage high-capacity pump and (b) the gases are determined volumetrically, by measuring the pressure in the system before and after each absorption.

TABLE 2.—*Determinations of the oxygen contents of eight steels*

Steel	Oxygen		Steel	Oxygen	
	Vacuum-fusion	Hydrogen-reduction		Vacuum-fusion	Hydrogen-reduction
	Percent	*Percent*		*Percent*	*Percent*
1	0.017	0.016	4	0.003	0.005
	.018	.015		.004	.005
2	.017	.019	5	.012	.009
	.018	.013		.011	.013
		.015	6	.007	.008
3	.017	.013		.007	.011
	.018	.019	7	.110	.065
		.016		.111	.062
		.013	8	.017	.009
				.018	.009

The vacuum-fusion results are in excellent agreement with those previously obtained from other samples of these steels, confirming the uniformity of the materials and permitting comparison of results obtained from the current samples with the values established by the cooperative analysis.

The results obtained in this investigation by the hydrogen-reduction method are consistently in better agreement with results by other methods than they are with those of Brower and Larsen who used the same method. We are unable to explain the apparent lack of reproducibility of results by the modified hydrogen-reduction method, as indicated by lack of agreement between our results (table 2) and those reported by Brower and Larsen (table 1). Our apparatus and procedure were patterned after theirs, but, on the same materials, their values for oxygen are considerably higher than ours. Further work is evidently needed to establish the reproducibility of results by this method and to explain the discrepancies between our results and those obtained by Brower and Larsen.

Our determinations by the modified hydrogen-reduction method, for steels 1 to 6, inclusive, are in very good agreement with the total oxygen values listed in table 1 but the determinations on samples 7 and 8 are lower than the total oxygen values. This indicates that the hydrogen-reduction procedure yielded correct values, although less precise than the vacuum-fusion determinations, for the total oxygen contents of steels 1 to 6 in spite of the fact that some of the oxygen in each of these steels is combined as SiO_2 and Al_2O_3. The data in table 1 show that most of the oxygen in steel 5 is present in the form of SiO_2, whereas the greater part of the small amount of oxygen in steel 4 is combined as Al_2O_3. Recovery of all of the oxygen in these

[4] H. C. Vacher and Louis Jordan, BS J. Research 7, 375 (1931) RP346.

two steels, and in steels 1, 2, 3, and 6, means that small amounts of SiO_2 and Al_2O_3 are completely reduced by the hydrogen-reduction procedure. The method therefore is a total oxygen method, at least for these six steels.

The data for steel 8 furnish further evidence of the reducibility of alumina in the hydrogen-reduction procedure, although in this case the amount of Al_2O_3 is relatively large and the reduction is incomplete. The data in table 1 show that practically all of the 0.017 percent of oxygen in steel 8 is present as Al_2O_3. The 0.009 percent of oxygen recovered by the hydrogen-reduction procedure must represent reduction of approximately half of the Al_2O_3 in this steel. It appears, therefore, that the hydrogen-reduction procedure reduces some Al_2O_3 but yields low results for oxygen in steels that contain considerable quantities of alumina. The size of the alumina particles presumably affects the rate of their reduction and the proportion of the total that is reduced; the finer particles would be more readily and more completely reduced than the larger ones. It would be expected that the reduction of large amounts of alumina would be less rapid and complete by hydrogen at 1,200° C in the hydrogen-reduction method than by carbon at 1,650° C in the vacuum-fusion method.

The low results for open-hearth iron, sample 7, were unexpected. It is known that most of the large amount of oxygen in this material is present as easily reducible iron oxide, and it would be expected that the hydrogen-reduction method would yield its best results in material of this type. It was suspected that the low recoveries from this sample might be caused by loss of body oxygen during the stripping procedure that is supposed to remove only the surface oxygen. Consequently experiments were undertaken to investigate this possibility.

A determination of both the surface oxygen and body oxygen on a sample of millings from iron 7 gave 0.069 percent of surface oxygen at 500° C, and 0.062 percent of body oxygen at 1,200° C, making a total of 0.131 percent. Another sample of the same millings was briquetted and analyzed for total oxygen by the vacuum-fusion method. The result, 0.138 percent of oxygen, shows good agreement between the two methods for determinations which in each case included both surface and body oxygen. If the vacuum-fusion value for oxygen in a solid sample (0.110 percent), is subtracted from the vacuum-fusion value for the milled sample (0.138 percent), the difference (0.028 percent), is of the usual order of magnitude of values for surface oxygen from millings of the plain carbon steels that were studied in this investigation. The fact that, in the hydrogen-reduction method, 0.069 percent of oxygen was removed at a stripping temperature of 500° C and only 0.062 percent was subsequently recovered at 1,200° C indicates that exposure of this iron to hydrogen at 500° C removes some of the body oxygen as well as the surface film. Even at 400° C the results for surface oxygen were high and for body oxygen were low. Therefore it was decided to study the stripping procedure over a range of temperatures for steels 1 (low-carbon rimming), 4 (aluminum-killed), 5 and 6 (silicon-killed), as well as for iron 7. The results of the determinations, in which the designated stripping temperatures were maintained for the regular period of 90 minutes with subsequent determinations of the body oxygen, are given in table 3.

TABLE 3.—*Effect of stripping temperature on the determination of surface and body oxygen by the hydrogen-reduction method*

Steel	Stripping temperature	Surface oxygen	Body oxygen	Sum of surface and body oxygen
	° C	*Percent*	*Percent*	*Percent*
1	400	0.021	0.017	0.038
	500		.015 [a] (.018)	
	550		.016	
	700	.018	.019	.037
4	200	.008	.014	.022
	300	.037	.008	.045
	400	.029	.004	.033
	500		.004 [a] (.002)	
	500		.005	
	550		.005	
	700	.014	.008	.022
5	300	.022	.007	.029
	300	.024	.006	.030
	500		.013 [a] (.009)	
	550		.009	
	700	.017	.015	.032
6	300	.028	.009	.037
	500		.008 [a] (.007)	
	500		.011	
	700	.018	.025	.043
	700	.020	.022	.042
7	300	.020	.096	.116
	400		.083	
	400		.083	
	500	.062	.065 [a] (.106)	.127
	500	.069	.062	.131
	700	.072	.053	.125

[a] Figures in parentheses are the values from table 1 for the oxygen contents of these steels. These values represent the oxygen *in* the steel; they do not include surface oxygen.

The relatively large surface area of these milled samples and the changes from day to day in the temperature and humidity of the atmosphere to which the millings had been exposed, might be expected to produce relatively large fluctuations in the values for surface oxygen from different samples. However, the values for surface oxygen lie quite consistently between 0.02 and 0.03 percent (except for iron 7) and the sum of body oxygen and surface oxygen stripped at different temperatures is fairly constant for each material.

Comparison of the determinations of body oxygen in table 3 with the values for oxygen contents of these steels, from table 1, show that quite satisfactory values for body oxygen are obtained from steels 1, 4, 5, and 6 after stripping the surface oxygen at 500 to 550° C, as was recommended by Brower, Larsen, and Shenk. The data further show that surface oxygen can be satisfactorily removed from these steels at any temperature between 400 and 550° C; stripping temperatures as low as 300° C may be used for steels 5 and 6, but 200° C is too low to remove the surface oxygen completely from steel 4, so that the subsequent determination of body oxygen is high. The surface oxygen may be stripped at 700° C from steel 1, but not from steels 4, 5, and 6. It might be anticipated that the use of too high a stripping temperature would lead to low recoveries in the subsequent determination of body oxygen at 1,200° C, because of reduction of some of the body oxygen during the stripping operation. However, this is not the case for steels 4, 5, and 6; for each of these and particularly for steel 6, stripping the surface oxygen at 700° C is followed

by high results for body oxygen. A possible explanation for this behavior lies in the fact that all three of these are killed steels. It is suggested that, in heating the millings to 700° C, some of the surface oxygen may react with metallic silicon of steels 5 and 6, or with aluminum of steel 4, becoming fixed in a form that is not reduced until the temperature is raised to 1,200° C. The combinations that comprise the body oxygen of these killed steels evidently are not reduced at stripping temperatures.

For any one of these four steels, therefore, the stripping operation can be conducted at any temperature within an appreciable range without seriously affecting the subsequent determinations of body oxygen. The data for iron 7, however, present a different picture. For this iron, with increasing stripping temperature there was a progressive increase in the amount of surface oxygen together with a progressive decrease in the amount of body oxygen subsequently recovered at 1,200° C. The highest value for body oxygen was obtained when a stripping temperature of 300° C was used, but even in this case the results for body oxygen were too low. Attention is also called to the unusually large values for surface oxygen, 0.06 and 0.07 percent, obtained from this iron at 500 and 700° C, in comparison with the usual value, 0.02 to 0.03 percent, for the surface oxygen of the four steels. These data indicate that a stripping operation at 500° C not only removes the surface oxygen but also reduces appreciable amounts of the body oxygen in open-hearth iron. It is probable that FeO inclusions are exposed in the surface of the millings and that some of this exposed FeO is reduced simultaneously with the surface oxides, not only at 500° C but at other temperatures as well. A stripping temperature at which the surface oxygen of this material could be satisfactorily separated from the body oxygen, could not be found. Consequently it appears that the modified hydrogen-reduction procedure is not applicable to the determination of oxygen in open-hearth iron.

IV. CONCLUSIONS

The Brower, Larsen, and Shenk modification of the hydrogen-reduction method yielded accurate results for the total oxygen contents of six plain carbon steels of the following ranges of composition: Carbon, 0.03 to 0.43 percent; silicon, 0.002 to 0.26 percent; manganese, 0.31 to 1.15 percent; and sulfur, 0.025 to 0.168 percent. The oxygen contents of these steels lie between 0.002 and 0.018 percent.

The fact that accurate values were obtained for silicon-killed steels indicates the reduction of some silicates by this method. Small amounts of alumina also were reduced but, for aluminum-killed steels that contain appreciable amounts of alumina, the hydrogen-reduction method gave low results for total oxygen.

The method is not applicable to the determination of oxygen in open-hearth iron that contains relatively large amounts of easily reducible iron oxide, because of inability to separate the surface oxygen from body oxygen in this material.

The precision of determinations by the modified hydrogen-reduction method for the determination of oxygen in steels, is usually of the order of ± 0.003 percent.

WASHINGTON, April 22, 1938.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1115

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DETERMINATIONS OF OXYGEN IN ALLOY STEELS

By John G. Thompson and Vernon C. F. Holm

ABSTRACT

The oxygen contents of many types of alloy steels can be determined with accuracy by either the vacuum-fusion or the hydrogen-reduction procedure. The presence of the common alloying elements does not interfere with the operation of either method. The limitations of both methods are essentially the same for alloy steels as for plain carbon steels.

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I. INTRODUCTION

The determination of the oxygen contained in any specimen of ferrous material is a complex problem because of the number of forms and combinations of oxygen that are encountered. Even the simplest of plain carbon steels may contain oxygen in three distinct states (*a*) gaseous compounds, (*b*) solid solution, and (*c*) inclusions. The amounts of the first two usually are of minor importance, the bulk of the oxygen occurring as simple or complex inclusions of FeO, MnO, SiO_2, and Al_2O_3. The relative proportions of the four oxides and their states of combination depend on the practice employed in the melting and refining of the steel. Each of these oxides and combinations presents different analytical problems, and the matter becomes increasingly complicated in alloy steels because of the probable occurrence of additional oxide compounds of the alloying elements.

The application of the various methods to the analysis of plain carbon steels has been extensively investigated, but the accuracy of the various methods, even for the analysis of simple steels, is still a controversial question in some respects. The report of the recent cooperative study of methods for the determination of oxygen in steel [1] [1] showed, by means of agreement in results obtained by different methods, that accurate determinations of Al_2O_3 in simple steels can be made by several methods; the accuracy of determinations of SiO_2 varies with the composition of the silicate inclusions; reliable

[1] The numbers in brackets here and throughout the text refer to the list of references at the end of the paper.

methods for the determination of FeO and MnO are not yet available; accurate determinations of total oxygen, without identification of the various oxides, can be obtained from many plain carbon steels by the vacuum-fusion procedure. This procedure may yield low results if the sample has a high content of manganese or other volatile metal, and particularly if large or refractory inclusions also are present. Recent work in this laboratory [2] has shown that a modified hydrogen-reduction method also yields accurate results for the total oxygen content of many plain carbon steels, although low recoveries of oxygen may be obtained if high contents of Al_2O_3 or FeO are present.

The determination of oxygen in alloy steels has received relatively little attention. A few determinations have been reported but no attempt has been made to define their accuracy, as was done for determinations on simple steels in the cooperative analysis. Ericson and Benedicks [3], in 1931, reported that satisfactory determinations of the oxygen content of low-carbon steel were obtained by means of their vacuum-fusion procedure, in spite of the presence in the crucible of alloying elements in amounts as follows: Up to 50 percent of chromium, 10 percent of tungsten or molybdenum, 2.5 percent of vanadium, and 1 percent of titanium. This lack of interference, by metallic alloying elements, in the determination of the oxides in a simple steel does not necessarily mean that the analysis of alloy steels would be equally satisfactory. Alloy steels may contain oxides of the alloying elements in addition to FeO, MnO, SiO_2, and Al_2O_3, and it is not definitely known whether these oxides of the alloying elements are more or less refractory than the oxides and combinations ordinarily encountered in simple steels.

Hamilton [4] reported that results for oxygen in certain alloy steels, by the vacuum-fusion method, were satisfactorily reproducible and could be correlated with certain properties of the steels. Reproducibility of results, however, does not establish their accuracy. The recent cooperative study [1] revealed a number of instances where different analysts using the same method could each duplicate their own results with satisfactory precision, but the reproducible results of one analyst were not in satisfactory agreement with the reproducible results of another. The best criterion of accuracy that is available at present, in the determination of oxygen, is agreement of results obtained by different methods of analysis.

II. PURPOSE OF THE INVESTIGATION

The present investigation is an attempt to establish the accuracy of oxygen determinations in alloy steels through the use of two independent methods of analysis. Residue methods were eliminated from consideration for two reasons: (a) Uncertainty of their reliability in the determination of oxides in simple steels and (b) uncertainty of their application to the determination of the other oxides presumably present in alloy steels. The two methods that were selected were the vacuum-fusion method, essentially as described by Vacher and Jordan [5], and a modification of the hydrogen-reduction method, essentially as described by Brower, Larsen, and Shenk [6]. In the vacuum-fusion procedure the oxides in the molten sample are reduced by carbon at 1,650° C, and the gaseous products of the reduc-

tion reactions are subsequently determined. In the modified hydrogen-reduction procedure the finely milled sample is treated with hydrogen, first at about 500° C to remove the surface film of oxides and moisture, and finally at 1,200° C to reduce the dissolved or "body" oxides of the sample. The products of the latter reduction reactions are subsequently recovered and determined.

The results obtained in the cooperative analysis [1] and in additional experiments in this laboratory [2] showed that both procedures determined total oxygen in simple steels and that, when determinations by the two methods were in agreement, the indicated values were close approximations of the true oxygen content of the steel. Each method has its limitations, but these are not the same for both. Consequently, in the analysis of alloy steels or other steels of unknown oxygen content, agreement in results obtained by these two independent methods is strong evidence of accuracy, and failure to obtain agreement indicates that one or the other method is in error.

III. EXPERIMENTAL RESULTS

Determinations of oxygen, by both the vacuum-fusion and hydrogen-reduction methods, were made on 14 alloy steels covering a wide range of composition of commercially important materials. Nine of the samples were prepared from material constituting some of the Bureau's Standard Samples and several additional samples of 18 chromium–8 nickel steel were included because of the current interest in this particular composition. The compositions of the steels are indicated in table 1.

TABLE 1.—*Composition of alloy steels*

Steel	Description	Alloying elements	C	Mn	Si	P	S
1	Standard Sample 33b	Ni 3.48	0.37	0.70	0.23	0.037	0.032
2	Standard Sample 32b	Ni 1.21; Cr 0.64	.41	.62	.22	.016	.018
3	Standard Sample 111	Ni 1.75; Cr 0.27; Mo 0.22	.20	.66	.29	.023	.020
4	Standard Sample 30c	Cr 0.98; V 0.24	.49	.71	.24	.019	.014
5	Standard Sample 73	Cr 13.9	.31	.28	.36	.023	.031
6	Standard Sample 50a	W 18.25; Cr 3.52; V 0.97	.66	.29	.48	.020	.007
7	18–8 Stainless	Cr 18.6; Ni 9.1	.07	.27			
8	do	Cr 18.5; Ni 9.2	.11	.19			
9	do	Cr 19.6; Ni 8.96	.24	.37			
10	do	Cr 19.6; Ni 7.99	.24	.28			
11	Standard Sample 106	Cr 1.29; Al 1.06; Mo 0.16	.34	.48	.25	.020	.019
12	Standard Sample 100 (Mn rail steel).		.62	1.38	.19	.023	.021
13	Standard Sample 101	Cr 17.6; Ni 8.44	.06	0.55	.76	.010	.013
14	18–8 Stainless	Cr 18.8; Ni 8.26	.10	.34	.49	.019	.023

The results of the determinations of oxygen are presented in table 2. Steels 1 to 10, inclusive, cover a wide range of compositions, for all of which satisfactory results were obtained by both methods of analysis. In the vacuum-fusion determinations there was no evidence of interference by any of these alloying elements. The determinations proceeded smoothly and without apparent difficulty; the precision, i. e., the reproducibility of results, is fully as good as for simple steels. The accuracy of these results is confirmed by the hydrogen-reduction determinations. The agreement between the results by the two methods is very good in most cases and even for steels 2 and 6 where

the accord is least satisfactory, the results are still in agreement within the combined tolerances of the two methods, ±0.002 percent for the vacuum-fusion method and ±0.003 percent for the hydrogen-reduction method.

TABLE 2.—*Determinations of oxygen in alloy steels*

Steel	Type	Oxygen by vacuum-fusion	Oxygen by hydrogen-reduction	Steel	Type	Oxygen by vacuum-fusion	Oxygen by hydrogen-reduction
		Percent	*Percent*			*Percent*	*Percent*
1	3.5 Ni	0.012 .011	0.012 .009	9	19 Cr; 9 Ni	.020 .020	.020 .018
2	1.2 Ni; 0.6 Cr	.006 .005	.011 .010	10	19 Cr; 8 Ni	.018 .020	.016 .016
3	1.7 Ni; 0.3 Cr; 0.2 Mo	.004 .004	.002 .002	11	1.3 Cr; 1.0 Al; 0.2 Mo	.002 .003	.000 .000
4	1.0 Cr; 0.2 V	.006 .005	.007 .009	12	1.4 Mn	.003 .003	.011 .009
5	14 Cr	.020 .018	.012 .017 .020	13	18 Cr; 8 Ni	.008 .009	.000 .004 .002 .005
6	18 W; 3.5 Cr; 1.0 V	.004 .004	.009 .006				.005 .006
7	18 Cr; 9 Ni	.011 .012	.014 .017	14	19 Cr; 8 Ni	.017 .018 .022	.012 .015 .016
8	18 Cr; 9 Ni	.013 .013	.014 .013				.008 .009

The data for steels 1 to 10, inclusive, therefore indicate that both the vacuum-fusion and hydrogen-reduction methods yield accurate results for samples of the compositions indicated, with greater precision in the vacuum-fusion determinations. The data for steels 11 to 14, however, show that neither of the methods is infallible for the analysis of all types of alloy steel.

The results obtained from steel 11 are unusual in that the results of the two methods are in excellent agreement, but, nevertheless, are incorrect. Agreement between results derived from independent methods usually is good evidence of accuracy; the chance that independent methods would be equally affected so that results by the two methods would be equally in error, usually is remote. However, steel 11 presents a case in which this is not true. The results of the vacuum-fusion and hydrogen-reduction methods are in good agreement and indicate that the oxygen content does not exceed 0.003 percent, but residue analyses by the hydrochloric acid method show that 0.011 percent of oxygen is present in the form of Al_2O_3. Microscopic examination reveals the presence of alumina inclusions arranged in the usual stringer formation, together with some large inclusions, as shown in figure 1(*A*). The large inclusions, up to 0.03 mm. in diameter, were angular in outline, suggesting a refractory, high-melting composition that was not elongated during previous hot- or cold-work. The inclusions were a light gray in color, similar to the color of FeO. At higher magnification, the presence of black lines within the inclusion, as shown in figure 1(*B*), indicates a duplex structure, although there were no differences in the appearance of the different portions of the inclusion, nor in their response to the action of chemical reagents. In the section shown in figure 1(*B*), the white areas within the inclusion are holes or thin spots that have been polished through,

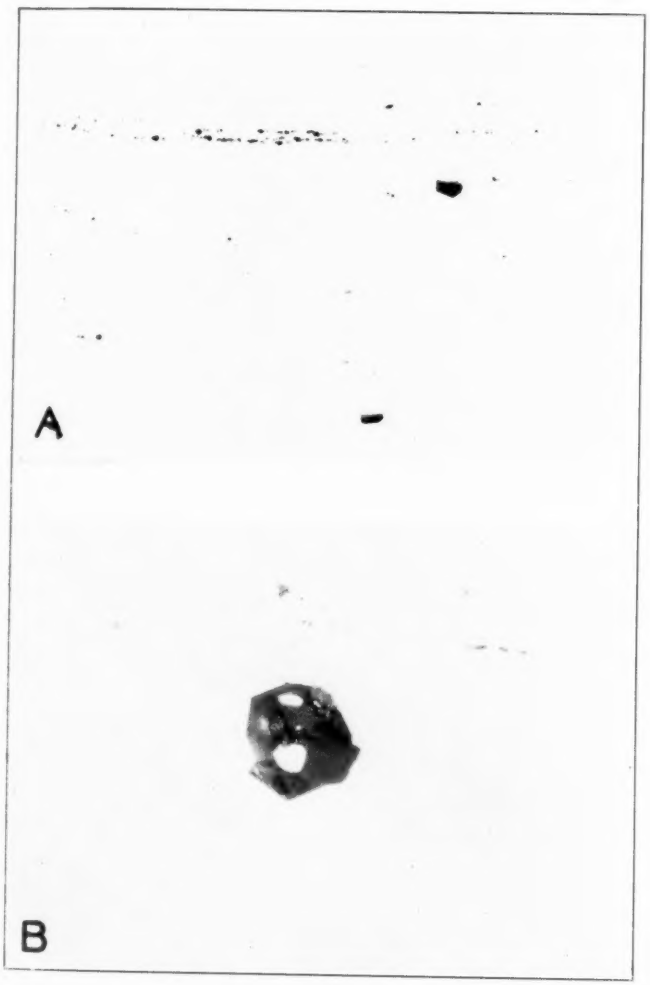

FIGURE 1.—*Inclusions in steel 11.*

A, Typical Al_2O_3 stringers and occasional large inclusions, ×100; *B*, appearance of one of the large inclusions at higher magnification, ×500.

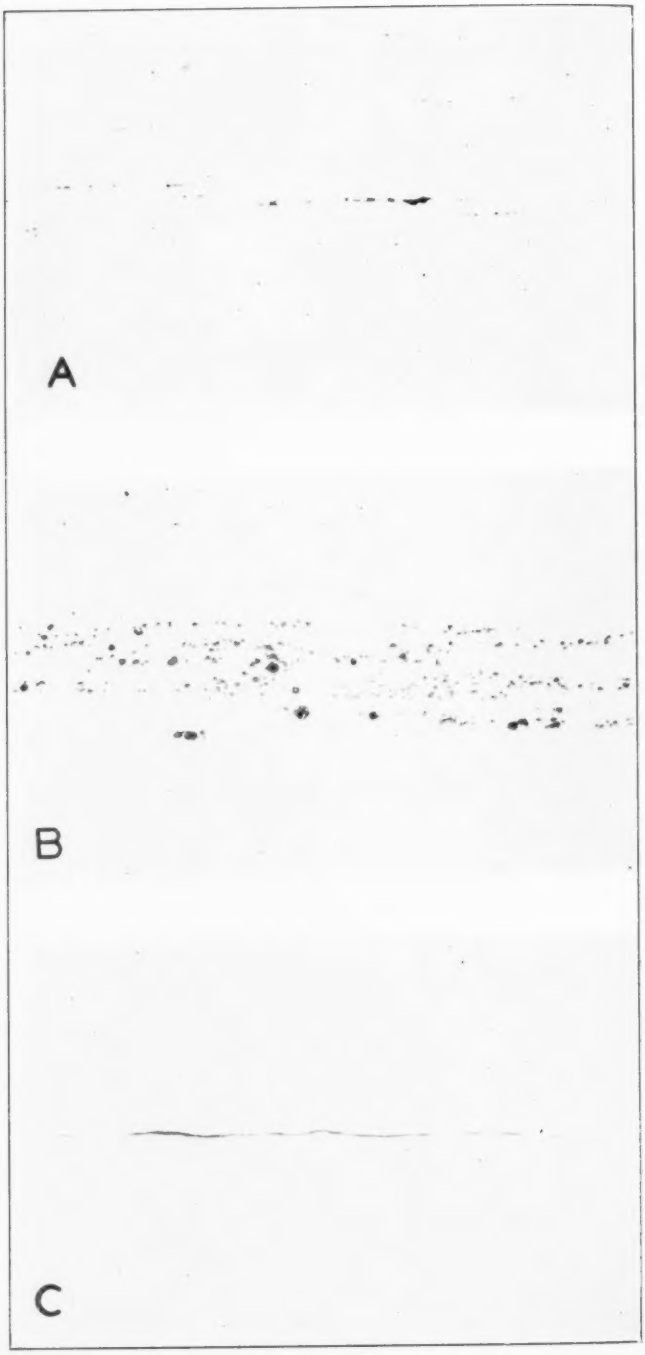

FIGURE 2.—*Inclusions in 18–8 steels.*

A, Typical appearance of steels 7 to 10, inclusive, ×100; *B*, inclusion band in steel 13, ×100; *C*, elongated inclusions in steel 14, ×100.

exposing the underlying iron. Identification of the large inclusions, by means of Campbell and Comstock's procedure as modified by Wohrman [7], was not conclusive.[2] They were not attacked by 10 percent nitric acid in alcohol nor by 10 percent chromic acid in water. They were slightly attacked by boiling alkaline sodium picrate, but subsequently were unaffected by a saturated solution of stannous chloride in alcohol. After a final treatment with hydrofluoric acid, which attacked the inclusions slightly, an attempt to repolish the specimen was made but was unsuccessful. The large inclusions evidently had been loosened by the various etchants and could not be retained in the specimen during repolishing.

These observations, together with the refractory composition evidenced by the failure to be elongated by previous work, suggest that the inclusions are rich in alumina, perhaps with small amounts of MnO and SiO_2 present. Furthermore, some of the large inclusions were intimately associated with groups or stringers of typical Al_2O_3 inclusions; in one case a stringer of Al_2O_3 appeared to be a tapering tail attached to one of the large inclusions. On the other hand, the appearance of the large inclusions differed from that of the small inclusions that are generally typical of Al_2O_3. However, Al_2O_3 inclusions of this size have not been generally observed nor widely studied. It is possible that the appearance of an Al_2O_3 particle of this size would differ appreciably from the appearance of the same material in a very fine state of subdivision.

It should be mentioned that the material for sample 11, and the other samples identified in table 1 as Standard Samples, was obtained from the cores that remained after most of each billet had been removed. Obviously any segregation in the ingot would be concentrated and intensified in the core. The micrographs shown in this paper represent the waste material that was not used in the preparation of standard samples; they do not represent the structure of the material actually used in the preparation of the Standard Samples issued by this Bureau.

The explanation for the low results for oxygen in steel 11, by both methods, presumably is found in the nature and size of the inclusions. It is known that reduction of Al_2O_3, particularly in large particles, is relatively slow in the vacuum-fusion procedure and that low recoveries of oxygen may be obtained from samples that, in addition to Al_2O_3, contain appreciable amounts of volatile metals such as manganese or aluminum. The low recovery of oxygen from steel 11, by the vacuum-fusion method, apparently illustrates interference by aluminum vapor coupled with slow reduction of the large particles of Al_2O_3. If particles of Al_2O_3 are reduced only slowly at 1,650° C, in the vacuum-fusion procedure, it would be expected that they would be reduced more slowly or not at all at 1,200° C, in the hydrogen-reduction procedure. The Al_2O_3 that exists in this steel evidently is not reduced by the hydrogen-reduction procedure.

The data for steel 12 also illustrate the interference of metal vapors, manganese in this case, in the operation of the vacuum-fusion method. Although this steel presumably was killed with aluminum (the total Al content is 0.02 percent), residue analyses show only 0.004 percent of Al_2O_3, equivalent to 0.002 percent of oxygen. Apparently oxides

[2] The preparation of metallographic specimens and the identification of inclusions were conducted by G. A. Ellinger and J. S. Acken.

other than Al_2O_3 are present in this steel and are reduced in both analytical procedures. In the vacuum-fusion procedure a secondary reaction with manganese vapor probably interfered with the recovery of the evolved oxygen, whereas the hydrogen-reduction procedure was not subject to this interference. This steel furnishes an unusual example in that the hydrogen-reduction results are higher and probably more nearly correct than the vacuum-fusion determinations.

For steels 13 and 14, both of the 18–8 type, unsatisfactory and erratic results were obtained, particularly by the hydrogen-reduction method. This is in distinct contrast to the results obtained for steels 7 to 10, where both analytical methods yielded satisfactory results of a high degree of precision. However, microscopic examination furnishes a clue to this variation in behavior of different steels of the same general type. Figure 2(A) is typical of the appearance of steels 7 to 10, inclusive, for which satisfactory analytical results were obtained. There are occasional oxide stringers, but most of the inclusions are very small and are uniformly distributed throughout the specimen. On the other hand, steel 13 contained broad bands of oxide inclusions, many of them of appreciable size, as is illustrated in figure 2(B). This condition could account for the low and somewhat erratic recoveries of oxygen by the hydrogen-reduction method because of slow and incomplete reduction of the large oxide particles. The values obtained by the vacuum-fusion procedure are higher and probably approximate more closely the true oxygen content of the steel.

For steel 14, the low and erratic results by the hydrogen-reduction method apparently are associated with the presence in this steel of elongated inclusions, probably silicates, illustrated in figure 2(C). It is obvious that, in the preparation of the very fine millings required in the hydrogen-reduction procedure, brittle inclusions of the type and size shown in figure 2(C) could be shattered and lost. Two of the determinations by the hydrogen-reduction method indicated 0.015 and 0.016 percent of oxygen, respectively, in fairly good agreement with the vacuum-fusion values. These two determinations probably were made on samples in which the inclusion material had been completely retained; the low and erratic values by the hydrogen-reduction procedure probably result from the loss of brittle inclusion material during the preparation of the finely milled sample. In the large, solid samples used in the vacuum-fusion procedure, there is less danger of loss of brittle inclusions. The higher and more consistent results by the vacuum-fusion procedure probably are better approximations of the oxygen content of this steel.

IV. SUMMARY

Agreement in results for oxygen in alloy steels, obtained by two independent methods of analysis, is evidence of the accuracy of the results obtained from a majority of the steels. It is known that either method, under certain conditions, may yield low results for oxygen. Consequently, if results by the two methods are not in agreement, the higher values are probably more nearly correct.

The vacuum-fusion method has been shown to yield accurate results for the oxygen contents of a number of alloy steels, representing a wide range in composition and type. Low recoveries of oxygen were

obtained from certain alloy steels because of interference by vapors of aluminum or manganese, particularly when the steels also contained difficultly reducible oxides. The evidence of the present work is that the vacuum-fusion method is equally applicable to, and is subject to the same limitations in, the analysis of alloy steels and of simple, plain carbon steels. The presence of the common alloying elements or their oxides does not present added difficulty in the operation of the vacuum-fusion method.

The hydrogen-reduction method likewise yields accurate results for a number of alloy steels. However, the precision of this method is not as good and the range of applicability is not as great as that of the vacuum-fusion method. Low recoveries of oxygen are obtained by the hydrogen-reduction method when appreciable quantities or large particles of Al_2O_3 are present; low and erratic results may be obtained when large inclusions other than Al_2O_3 are present. On the other hand, the hydrogen-reduction procedure is not as susceptible to manganese interference as is the vacuum-fusion procedure.

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DETERMINATION OF ARSENIC, ANTIMONY, AND TIN IN LEAD-, TIN-, AND COPPER-BASE ALLOYS

By John A. Scherrer

ABSTRACT

A method is described in which arsenic, antimony, and tin are separated from most of the lead in babbitts, type metals, solders, and the like, by digestion in hydrofluoric, nitric, and sulfuric acids, and from most of the copper, zinc, lead, etc., in brasses and bronzes by digestion in nitric acid, or precipitation by ammonium hydroxide. The three elements are then converted to sulfates, the arsenic and antimony reduced to the trivalent state, and the three then separated by fractional distillation and determined by titration.

When tin and antimony are titrated in solutions of lead-tin-antimony-copper alloys, obtained by dissolving the alloys in sulfuric acid-potassium sulfate, the results for antimony are usually high and for tin usually low.

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I. INTRODUCTION

The determination of antimony and of tin in lead-base and in tin-base alloys is usually made by titration with an oxidizing reagent in a solution of the alloy in sulfuric and hydrochloric acids. In the case of brasses and bronzes whose iron content is low, tin together with antimony and arsenic, if the alloy contains a sufficient proportion of tin, are usually first separated from other constituents by digesting the alloy with nitric acid and filtering the resulting solution. The filter paper and precipitate are decomposed by heating with sulfuric

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and nitric acids, and then the antimony and tin are determined by titration. Arsenic is usually determined by titration after it has been distilled from the solution of a separate sample. Methods of the type just mentioned are subject to a number of limitations. For example, in the determination of antimony by titration with permanganate correction must be made for arsenic. The titration of antimony and tin in the presence of some of the other constituents of these alloys yields values which are usually high for antimony and low for tin. For purposes of rapid control such determinations are satisfactory, except when relatively small amounts of antimony (up to about 20 mg) are involved. In this instance the result for the determination of antimony may be high by two- or threefold.

If, however, arsenic, antimony and tin are successively removed from solution by distillation as recommended by Scherrer [1] and subsequently titrated, they can be accurately determined.

With lead-base alloys it is necessary first to eliminate most of the lead either as sulfate or chloride. Clarke, Wooten, and Struthers [2] have described an extraction apparatus for this purpose which is especially useful when a large amount of alloy must be taken.

In the customary procedures for the removal of lead as sulfate, the precipitate retains more or less of the antimony, tin, and arsenic, but if the lead sulfate is precipitated in the presence of hydrofluoric acid only traces of these elements are retained.

II. PROCEDURE RECOMMENDED FOR THE DETERMINATION OF ARSENIC, ANTIMONY, AND TIN

1. IN BABBITT METALS, TYPE METALS, AND SOLDERS

(a) PREPARATION OF THE SOLUTION

The quantity of the sample taken should be such that the amount of antimony does not exceed 100 mg, the amount of tin not more than 200 mg, and the quantity of lead not greater than 5 g. If the amounts of antimony and tin are very small, it is best to take several 5-g portions and remove the lead from each such portion. The volume of sulfuric acid in the combined resulting solutions should not exceed about 10 ml.

Place the sample in a 200-ml platinum dish, provided with a platinum or gold cover, add 50 ml of water, 10 ml of nitric acid [3] and 10 ml of hydrofluoric acid, and heat on the steam bath. When the alloy is completely dissolved, wash and remove the cover, and continue to heat the solution for about 5 minutes, or until oxides of nitrogen are no longer evolved. Remove the dish from the steam bath and add cautiously 16 ml of diluted sulfuric acid (1+1). Stir thoroughly with a platinum stirring rod or wire, or by twirling, and set aside for 30 minutes or more. Filter through a 9-cm filter paper on a hard-rubber funnel and catch the filtrate in a platinum dish. Wash the lead sul-

[1] J. A. Scherrer, J. Research NBS **16,** 253–259 (1936) RP871.
[2] Ind. Eng. Chem. Anal. Ed. **29,** 349 (1937).
[3] Throughout this paper whenever acids are mentioned, nitric acid will mean the concentrated acid of specific gravity 1.42; hydrochloric acid, the concentrated acid of specific gravity 1.18; sulfuric acid, the concentrated acid of specific gravity 1.84; phosphoric acid, the acid containing 85 percent of H_3PO_4; hydrofluoric acid, the acid containing 48 percent of HF; acetic acid, the glacial acid containing 99.5 percent of acetic acid; hydrobromic acid, the concentrated acid containing 48 percent of HBr; and ammonium hydroxide, the concentrated ammonium hydroxide of specific gravity of 0.90. Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+99) will mean 1 part of the concentrated acid of specific gravity 1.18 diluted with 99 parts of water.

fate with 5-ml portions of a solution consisting of 25 ml of distilled water, 5 ml of nitric acid, 5 ml of hydrofluoric acid and 2 ml of sulfuric acid, and contained in a platinum or ceresin vessel. Finally, wash twice with water. Evaporate the filtrate and washings in a platinum dish on the steam bath.

To recover any arsenic, antimony, or tin in the precipitate, remove the paper from the funnel, and sluice the lead sulfate into a 400-ml beaker, using as little water as possible.

Add 20 ml of hydrochloric acid, while agitating vigorously,[4] to convert the lead sulfate to lead chloride. Add enough of a 40-percent solution of sodium hydroxide (about 20 ml is usually required) to render the solution alkaline and to dissolve the lead chloride completely. Then, while stirring vigorously, add 20 ml of a 25-percent solution of yellow sodium sulfide.[5] Dilute to about 300 ml with distilled water and digest on the steam bath for at least 1 hour. Filter the solution, and wash the precipitate with a 2-percent solution of the yellow sodium sulfide. Discard the precipitate. Neutralize the filtrate with acetic acid, add 5 ml in excess, and treat with hydrogen sulfide for 5 to 10 minutes. Allow the solution to stand at room temperature for several hours, or overnight. Filter it through a paper, and wash the precipitate with a 1-percent solution of acetic acid saturated with hydrogen sulfide. Reserve the paper and precipitate.

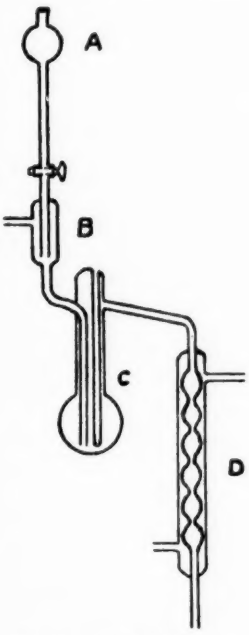

FIGURE 1.—*Distillation apparatus.*

Heat the main solution from which lead sulfate was removed just to fumes of sulfuric acid. Cool somewhat, wash down the sides of the dish, and again heat the sulfuric acid just to fuming to expel any remaining hydrofluoric acid. Transfer the solution to a Kjeldahl, flask with as little water as possible. Heat the solution over a free flame, while agitating it constantly until the water has evaporated. Add the reserved filter paper and precipitate. Let it stand for a few minutes to disintegrate the paper, and add about 25 ml of nitric acid. Heat over a direct flame with constant agitation. When most of the nitric acid has been expelled and the solution becomes straw yellow, add cautiously a few milliliters of nitric acid, and continue the heating and agitation until the nitric acid is expelled and fumes of sulfuric acid appear. If the solution darkens, continue the addition of small amounts of nitric acid and the heating until the organic matter is destroyed and the fuming sulfuric acid is colorless, or nearly so.[6] Cool somewhat, add

[4] Constant agitation of the lead sulfate during the addition of the hydrochloric acid results in a granular precipitate of lead chloride which does not cake and which dissolves readily in sodium hydroxide. The addition of hydrochloric acid to the lead sulfate facilitates its solution, and the sodium chloride which is formed is desirable as an electrolyte.

[5] The solution of yellow sodium sulfide is prepared as follows: Dissolve 250 g of colorless sodium sulfide in 1 liter of distilled water. If the solution is not perfectly clear, allow it to stand for several days and siphon off the clear liquid, add about 20 g of flowers of sulfur and allow to stand with occasional shaking until the solution has a bright yellow color.

[6] If iron, copper, or other elements forming colored ions are present, the sulfuric acid will not be entirely colorless. In such cases the treatment must be continued until no further change of color takes place.

cautiously about 10 ml of distilled water [7] and evaporate again until fumes of sulfuric acid appear. Add about 0.2 g of flowers of sulfur to the sulfuric acid solution and boil gently for about 10 minutes to reduce the arsenic and antimony to the trivalent state.[8] Cool, add about 25 ml of distilled water and 10 ml of hydrochloric acid. Stir to completely dissolve the compounds of arsenic, antimony and tin. Filter the solution through a paper of coarse texture and wash with about 20 ml of diluted hydrochloric acid (1+1). Transfer the solution to the all-glass distilling apparatus (fig. 1), wash the container with 40 ml of hydrochloric acid, and proceed with the distillation and determination of arsenic, antimony and tin, as described in section II, 4 and 5.

2. IN TIN-BASE ALLOYS

(a) PREPARATION OF THE SOLUTION

The following procedure is designed for the determination of arsenic, antimony, and tin in tin-antimony alloys which contain little or no lead. The sample taken should not contain more than 100 mg of antimony or 200 mg of tin. When only antimony is to be determined, the sample may contain as much as 0.5 g of tin. Greater amounts of tin than this tend to separate as tin phosphate during the distillation, and prevent complete distillation of antimony.

Place the sample in a 300-ml Kjeldahl flask, cautiously add 20 ml of nitric acid (1+1), and heat until the alloy is decomposed. Cool, add 8 ml of sulfuric acid, and heat over a free flame with constant shaking until the nitric acid is removed and vapors of sulfuric acid are evolved. When cool, add about 10 ml of distilled water (see footnote 7), and again heat until the water is expelled. Add a small amount of flowers of sulfur and boil for about 10 minutes. Cool the solution, add 25 ml of distilled water and 10 ml of hydrochloric acid. Stir to dissolve the compounds of arsenic, antimony, and tin. Filter the solution through a rapid filter paper to remove the sulfur. Wash the beaker and filter paper with 30 ml of diluted hydrochloric acid (1+1), added in 4 or 5 portions. Transfer the solution to the all-glass distilling apparatus (fig. 1) with enough hydrochloric acid to bring the volume to about 100 ml, and distill and titrate as described in section II, 4 and 5.

3. IN COPPER-BASE ALLOYS

(a) PREPARATION OF THE SOLUTION

For the complete separation of antimony and arsenic along with tin by nitric acid digestion, the tin must be at least 10 times as much as the total amount of antimony and arsenic. If the proportion is less than this pure tin may be added. Since 500 mg of tin is the maximum quantity which is permissible in the distillation of arsenic and antimony the total amount of these elements cannot exceed 50 mg. If tin, also, is to be separated by distillation it should not exceed about 200 mg.

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[7] The water is added at this point to aid the removal of oxides of nitrogen which are generally present when sulfuric acid solutions containing nitric acid are evaporated.

[8] The entire operation may becarried out in a beaker, if desired.

Place from 1 to 5 g of the alloy in a 250-ml beaker, provided with a cover, and add 20 to 50 ml of diluted nitric acid (1+1). Boil the solution to expel oxides of nitrogen, dilute to 150 ml with hot water, and allow it to stand on the steam bath for several hours, or overnight. Filter the solution through a paper of close texture and wash the precipitate with hot diluted nitric acid (1+99).[9] Place the paper and precipitate in a Kjeldahl flask, and proceed with the destruction of the paper, solution of the precipitate, and reduction with sulfur as in section II, 1 (a). Transfer the solution to the all-glass distilling apparatus (fig. 1) with enough hydrochloric acid to bring the volume to about 100 ml, distill and titrate as described in section II, 4 and 5.

The separation may also be made as follows: Dissolve the sample in aqua regia, and precipitate the arsenic, antimony, tin, etc., by ammonium hydroxide and proceed as described in footnote 9. The aqua regia must not be heated to more than incipient boiling in order to avoid loss of the elements to be determined.

4. DISTILLATION OF ARSENIC, ANTIMONY, AND TIN

(a) DISTILLING APPARATUS

In figure 1, *A* is a 50-ml bulb for holding the acid which is added in the course of the distillations. The tube connecting *A* and *B*, and extending into *B*, is 25 cm long, in order to overcome the pressure of the carbon dioxide which is used to aid in carrying over the vapors from the distilling flask *C*. The part of this tube extending into *B* should have a diameter of not over 3 or 4 mm in order to prevent the acid from draining from it.

B is an arrangement for gaging the rate of flow of the acid, and is provided with a side tube for the purpose of introducing a stream of carbon dioxide.

C is a 200-ml distilling flask, the neck of which is 2.5 cm in diameter. It is provided with a side tube, a thermometer well, and a delivery tube for conveying the acids and carbon dioxide to the distilling flask. The side tube connects the apparatus to a condenser, the thermometer well is sealed to the top of the neck of the flask, and the delivery tube passes through the wall in the upper part of the neck of the flask and is connected to *B*. Both the thermometer well and the delivery tube reach to within 3 mm of the bottom of the flask. The distance between the bottom of the flask and the exit tube leading to the condenser is 17 cm.

The apparatus is clamped to a ring stand. *C* rests on an asbestos board (about 18 by 18 cm) having a round hole 4.0 cm in diameter.

It is desirable that all the glass should be free from the elements in question, and the suitability of the apparatus for the work in hand should be determined by running appropriate blanks.

(b) DISTILLATION OF ARSENIC

Insert the thermometer in the well, and provide a receiver containing 50 to 100 ml of distilled water into which the end of the condenser

[9] If there is an appreciable amount of iron (1 mg or more) in the sample the precipitation of tin, etc., will not be complete. To recover it add ammonium hydroxide to the filtrate until it is strongly alkaline, boil, filter, and wash with diluted ammonium hydroxide (1+10). Add the paper and precipitate to the Kjeldahl flask in which the original paper and precipitate were placed. If the quantity of lead exceeds 1 percent, the ammonium hydroxide precipitate should be dissolved in nitric-hydrofluoric acids and lead separated as sulfate as in section II, 1 (a), and any arsenic, antimony, and tin which are recovered added to the Kjeldahl flask with the main precipitate.

dips. Pass a stream of carbon dioxide through the apparatus at the rate of about six to eight bubbles per second, heat the solution to boiling and boil gently until the volume in the distilling flask has been reduced to 50 ml. The rate of flow of the carbon dioxide should be regulated so that the temperature will be 110 to 111° C at this stage. Without interrupting the stream of carbon dioxide or the heating, remove the receiver and rinse the end of the condenser with distilled water. Reserve the distillate for the determination of arsenic, and place another receiver containing 50 to 100 ml of distilled water in position.

One distillation usually suffices if the amount of arsenic does not exceed 0.001 g. If larger amounts are in question, it is advisable to add 25 ml or more of the acid and repeat the distillation. In analyses of the highest accuracy, especially if the amount of antimony is large, the arsenic should be redistilled, as a few tenths of a milligram of antimony may distill over with the arsenic. In this case transfer the distillate to an empty distilling flask, and again distill until the volume in the flask is reduced to 50 ml. Then add 25 ml of hydrochloric acid and continue the distillation until the residue in the flask is again reduced to 50 ml. Add the residual solution to the residue left in the first distilling flask.

(c) DISTILLATION OF ANTIMONY

Add 7 ml of phosphoric acid to the distilling flask, reduce the flow of carbon dioxide somewhat, and increase the rate of heating gradually until the temperature in the flask reaches 155° C. Then introduce hydrochloric acid from bulb *A* at a rate of 30 to 40 drops per minute, keeping the temperature in the flask between 155 and 165° C. One hundred mg of antimony requires 150 to 175 ml of hydrochloric acid. When all the antimony has been distilled, remove the burner, rinse the end of the condenser, change the receiver for another, and reserve the distillate for the determination of antimony.

(d) DISTILLATION OF TIN

Allow the solution in C to cool to 140° C, return the burner, and add a mixture of three-fourths hydrochloric acid and one-fourth hydrobromic acid to bulb *A*, allowing it to flow into the distilling flask at a rate of 30 to 40 drops per minute, and resume distillation, keeping the temperature at about 140° C. One hundred mg of tin requires about 125 ml of the mixed acid. When the distillation is finished, rinse the end of the condenser, and reserve the distillate for the determination of tin.

5. DETERMINATION OF ARSENIC, ANTIMONY, AND TIN

Determine the elements in the distillate as follows:

(a) ARSENIC

Neutralize the cold distillate with sodium hydroxide, acidify slightly with hydrochloric acid, and cool to room temperature. Then neutralize it with a saturated solution of sodium bicarbonate and add an excess of 20 ml. Titrate the arsenic with a standard solution of 0.01 *N* iodine, using a solution of starch as indicator. Make a

careful blank run on the same amounts of reagents as were used with the sample, adding 0.1 g of potassium iodide before titrating, and apply the correction obtained. The iodine solution should be standardized with pure arsenic trioxide.

(b) ANTIMONY

Neutralize the distillate with ammonium hydroxide and add 3 ml of hydrochloric acid for each 100 ml of solution. Pass hydrogen sulfide through the solution for 15 minutes. Allow the solution to stand for about 30 minutes and filter it. Wash the precipitate with a solution of diluted sulfuric acid (2+98), saturated with hydrogen sulfide. Transfer the paper and precipitate to a Kjeldahl flask, add 10 ml of sulfuric acid, allow it to stand a few minutes, then add about 25 ml of nitric acid, and destroy organic matter and reduce the antimony as described in section II, 1 (a). When the sulfuric acid solution has been boiled with sulfur for about 10 minutes, cool it, add 30 ml of distilled water and boil it until about one-half of the water has been evaporated, to remove sulfur dioxide. Add 25 ml of distilled water and 10 ml of hydrochloric acid, mix thoroughly and pass the solution through a rapid filter paper. Rinse the flask and paper with 60 ml of diluted hydrochloric acid (1+3), added in 4 or 5 portions. (A total of 25 ml of hydrochloric acid should be used.) Dilute the solution in the flask to 300 ml, boil it for about 5 minutes, cool to 10° C, and titrate the antimony with a standard solution of 0.1 *N* potassium permanganate. The permanganate solution may be standardized against pure antimony or standard sodium oxalate.

(c) TIN

Transfer the distillate to an Erlenmeyer flask and add distilled water until the solution contains approximately 30 percent of hydrochloric and hydrobromic acids (by volume). Reduce the tin by boiling it for 30 minutes with an excess of test lead. Cool the solution to 10° C and titrate with a standard solution of 0.1 *N* iodine, using a solution of starch as indicator. Pass a stream of carbon dioxide through the apparatus [10] during the reduction, cooling, and titration. The iodine solution should be standardized with weighed portions of pure tin by the procedure used for the sample.

III. DISCUSSION OF RESULTS

The data given in table 1 show that accurate results for arsenic, antimony, and tin are obtained by method *A* when applied to synthetic mixtures representative of lead-base bearing alloys. The amounts of arsenic, antimony, and tin retained by the lead sulfate, even when 5 g of lead is present, may be disregarded, except in analyses of the highest accuracy. In two experiments, the total recovery of arsenic, antimony, and tin was of the order of 0.2 mg in one case, and 0.1 in the other. When no hydrofluoric acid was used recoveries ranged from 2 to 4 mg.

The data in table 2 show that correct results for antimony in synthetic mixtures simulating tin-base alloys are obtained by method *B*.

[10] J. A. Scherrer, *Determination of tin in irons and steels*, BS J. Research 8, 309 (1932) RP415.

TABLE 1.—*Results obtained by applying method A to solutions of synthetic mixtures of the metals*

Arsenic		Antimony		Tin		Lead (taken)
Taken	Recovered [a]	Taken	Recovered [a]	Taken	Recovered [a]	
g	g	g	g	g	g	g
0.0010	0.0011	0.1064	0.1063	0.1136	0.1136	0.8
.0010	.0009	.1081	.1080	.1094	.1093	.8
.0020	.0019	.1080	.1081	.1229	.1230	.8
.0100	.0102	.1202	.1199	.1212	.1209	.8
.0200	.0199	.1083	.1085	.1283	.1283	.8

[a] These include such amounts of the element as were caught and recovered from the lead sulfate precipitate. In separate experiments it was determined that the total amount of the elements caught rarely exceeded 0.2 mg.

TABLE 2.—*Results obtained for antimony by applying method B to synthetic mixtures of antimony and tin (no lead present)*

Antimony		Tin (taken)
Added	Recovered	
g	g	g
0.0599	0.0600	0.5
.1025	.1025	.5
.0512	.0513	.5
.1032	.1010	[a] 2.0
.0278	.0271	[a] 2.5
.0523	.0518	[a] 2.5

[a] These 3 determinations show that tin should not exceed 0.5 g.

The reduction of arsenic and antimony by sulfur is rapid, and the excess of sulfur can be removed by filtration. Other reducing agents such as ferrous sulfate, cuprous chloride, potassium bromide, phosphorous acid, or organic substances (such as filter paper,[11] tartaric acid, and hydrazine sulfate), have been used in special cases. Under certain conditions, some of these, for example, phosphorous acid and hydrazine sulfate, reduce arsenic compounds to the metallic state. Bromides, which are sometimes added along with hydrazine sulfate and other reducing agents, must not be present when antimony and tin are to be separated, since even small amounts of hydrobromic acid cause tin to distill partially with the antimony. Ferrous sulfate and cuprous chloride can be used to reduce arsenic if it is determined in a separate sample.

If tin and antimony are titrated in solutions of alloys which contain lead, tin, antimony, and copper, obtained by dissolving the alloys in sulfuric acid and potassium sulfate, the results for antimony are usually high and for tin usually low. This is demonstrated by the data given in tables 3 and 4. Similar effects have been observed in experiments on the titration of antimony in synthetic mixtures of

[11] In the author's experience, reduction by means of filter paper is not satisfactory.

high-purity lead, tin, and antimony. For example, when the direct titration for antimony (footnote b, table 3) was applied to a mixture of 20 mg of antimony and 1 g of lead, the results obtained for antimony were consistently 1 to 2 mg too high. The same positive error was obtained, in the presence of lead, when the solution was first oxidized with permanganate, prior to reduction with sulfur. On the other hand, when the direct titration procedure for antimony (footnote b, table 3) was applied to a mixture of 100 mg each of antimony and high-purity copper, the results (blank for copper deducted) were about 1 mg low.

TABLE 3.—*Comparison of the results obtained in the analysis of white metals by method A and by direct titration*

Material	Antimony		Tin		Remarks
	Method *A* distillation procedure [a]	Direct titration [b]	Method *A* distillation procedure [a]	Direct titration [c]	
	%	%	%	%	
Pb-Sn solder *A*	0.064	0.17	----------	-----	2.5-g sample for method *A*. 0.05% As present.
Pb-Sn solder *B*	.13	.22	----------	-----	1-g sample for method *A*. 0.06% As present.
Pb-Sn solder *C*	.29	.41	----------	-----	2.5-g sample for method *A*. 0.04% As present.
Pb-Sb alloy	.81	.88	----------	-----	5-g sample for method *A*. 0.05% As present.
Lead-base bearing metal.	10.28	10.34	10.22	10.12	Pb=79.35; As=0.07; small amounts of Bi, Ag, Fe, Ni, and Cu.

[a] The completeness of the distillations of antimony and tin was checked, by changing receivers, adding more hydrochloric and hydrochloric-hydrobromic acids, respectively, and testing the distillates obtained. No antimony or tin was detected.

[b] Sample decomposed in sulfuric acid and potassium sulfate, and 275 ml of water and 25 ml of hydrochloric acid added. Solution boiled, cooled, and titrated with potassium permanganate. Apparent percentage of antimony corrected for arsenic by multiplying the percentage of arsenic (obtained on a separate sample) by 1.86 and deducting.

[c] Solution from the antimony titration, footnote b, treated with 80 ml of hydrochloric acid, reduced with test lead, cooled, and titrated in the presence of carbon dioxide with iodine.

TABLE 4.—*Comparison of the results obtained in the analysis of Ounce Metal by method C and by titration without separation of antimony and tin by distillation*

Antimony		Tin		Remarks
Method *C* distillation procedure	Titration without distillation [a]	Method *C* distillation procedure	Titration without distillation [b]	
%	%	%	%	This sample also contains approx. 84% of Cu, 5.5% of Zn; 4.8% of Pb; 0.45% of Ni; 0.37% of iron and small amount of Si, S, and P. (As not detected.)
0.222	0.24	4.68	4.55	
.224	.26	4.67	4.63	
.227	.22	4.69	4.58	
.228	.23	4.70	4.60	
Average.. 0.225	0.24	4.69	4.59	

[a] Alloy treated with diluted nitric acid and the residue of antimony, tin, arsenic, etc., filtered off and reserved. The filtrate was treated with ammonium hydroxide and the precipitate together with the first residue then treated with sulfuric-nitric acids, the solution diluted and titrated with permanganate after adding hydrochloric acid, boiling, and cooling.

[b] Solution from the antimony titration, footnote a, reduced with test lead and titrated with iodine.

Tests on the determination of tin in a synthetic mixture of 100 mg of copper, and 800 mg of lead, made by dissolving the metals in sulfuric acid, reducing with test lead, and titrating with iodine (footnote c, table 3) yielded results for tin that were about 1 mg low. With mixtures of only tin and antimony, both of high purity, correct results were obtained for both by direct titration (footnotes b and c, table 3).

Determinations of arsenic in lead-base and tin-base alloys, made by decomposing the samples in sulfuric acid and then separating the arsenic by distillation, yielded accurate results, showing that no arsenic is lost during the initial solution in the concentrated acid.

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IMPROVED METHOD FOR DETERMINATION OF ALUMINUM IN CERTAIN NONFERROUS MATERIALS BY USE OF AMMONIUM AURINTRICARBOXYLATE

By John A. Scherrer and William D. Mogerman

ABSTRACT

The difficulties encountered in using existing colorimetric methods for the determination of small amounts of aluminum in nonferrous materials are discussed. A method is proposed for obviating these difficulties. If the method is combined with a preliminary electrolysis in a mercury cathode cell, from 0.02 to 0.08 mg of aluminum can be determined quickly and accurately, without a colorimeter. The use of the mercury cathode cell and the effect of interfering substances are also discussed.

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I. INTRODUCTION

The determination of small amounts of aluminum has become a matter of considerable importance in the nonferrous and other metal industries. The undesirable effect of this element, even in very small amounts, in solders, bearing metals, and similar products makes it necessary for the buyer to limit the aluminum content rigorously. Thus, Federal Specification QQ–S–571, Tin-Lead Solder, Grade A, requires that the aluminum content shall be "none" on a 5-g sample. Federal Specification QQ–M–161, Anti-friction Metal, Grade 1, requires that the aluminum content shall be "none" on a 20-g sample. The increasing use of reclaimed metal has made these restrictions more necessary than ever.

Probably the best-known reagent for determining very small amounts of aluminum is ammonium aurintricarboxylate. The outstanding advantage which it has over other organic reagents for small amounts of aluminum is the almost complete absence of color when added in excess under the conditions of test. Thus, complicated formulas for correcting the determination are obviated.

Ever since this reagent was first recommended by Hammett and Sottery,[1] the method has been the subject of considerable research. Nevertheless, serious difficulties remain and have stood in the way of its general acceptance. The difficulties encountered in trying to apply the method to the routine requirements of a busy nonferrous analytical laboratory led to the work embodied in this paper.

The first difficulty is that the ammonium aurintricarboxylate generally available on the market is not satisfactory.[2] Scherrer and Smith [3] have eliminated this defect by preparing the reagent in a new way, but there still remains a serious drawback. Even with a good reagent, standards prepared by the usual procedures vary considerably and fade rapidly, duplicates disagree, blanks are not uniform, and results are generally inconsistent. It is, for instance, not at all uncommon to have a standard prepared from 0.03 mg of aluminum look darker than one prepared from 0.05 mg. Other investigators [4] have pointed out some of these defects, but the methods that have been proposed to overcome them are uncertain, complicated, and decidedly exacting.

The advantages of the method now proposed are speed, accuracy, extreme simplicity, and the use of no special apparatus. It consists essentially in subjecting a dilute sulfuric acid solution of the material to a treatment in a mercury cathode cell to remove interfering elements, and then determining aluminum colorimetrically in the filtered electrolyte.

II. MERCURY CATHODE CELL

The bulk of all interfering elements must be removed before the colorimetric test can be made. Removal by use of hydrogen sulfide or other chemical means is obviously undesirable because, with the small amounts of aluminum in question, effects such as adsorption and coprecipitation may cause loss of most of it in the preliminary work. Electrolysis in a mercury cathode cell was decided upon as the best way to remove many of the interfering elements. A modified Melaven cell [5] with a motor stirrer, as shown in figure 1, was used. Vigorous stirring of the mercury and solution are essential for rapid deposition. About 50 ml (650 g) of mercury and a current of 3 to 5 amperes was found suitable. Of course, the current permissible will vary with the size and shape of the cell, but in general, the highest current density which will not cause boiling of the solution and excessive spray may be used. Under these conditions 1 g of copper or of iron can be deposited completely in the mercury cathode in 35 to 45 minutes. Tin, antimony, lead, zinc, etc., take longer, but, depending upon the condition of the mercury, electrolysis for 2 to 3 hours will remove 1 g of any of these metals.

In the case of alloys such as solders, bearing metals, and bronzes, it was at first thought advisable to remove those metals which form peroxides (lead, bismuth, manganese) by depositing them on the anode instead of in the mercury cathode. To accomplish this a large platinum gauze anode was used. It was subsequently found that by using

[1] J. Am. Chem. Soc. **47**, 142 (1925).
[2] Under the conditions of test, a satisfactory reagent gives a definite pink color with 0.02 mg of aluminum and a slightly straw-colored blank with no aluminum in 50 ml of solution.
[3] J. Research NBS **21**, 113 (1938) RP1118.
[4] Winter, Thrun, and Bird, J. Am. Chem. Soc. **51**, 2721 (1929); also Cox, Schwartze, Hann, Unangst and Neal, Ind. Eng. Chem. **24**, 403 (1932).
[5] Ind. Eng. Chem., Anal. Ed. **2**, 180 (1930).

a platinum wire as anode (about 0.10 cm in diameter), which projected about 12 cm into the solution, a sufficiently high current density was established to prevent deposition of lead and bismuth as peroxides, and to cause them finally to collect in the mercury cathode. Under these conditions, much of the manganese is likewise deposited in the cathode.

It is known that iron, copper, nickel, cobalt, zinc, gallium, germanium, silver, cadmium, indium, tin, antimony, chromium, molybdenum, lead, bismuth, arsenic, selenium, tellurium, rhenium, osmium, thallium, mercury, gold, platinum, iridium, rhodium, and palladium can be completely deposited or removed electrolytically. Manganese is not removed entirely, but the small amount left in solution does no harm in the subsequent colorimetric test. Beryllium, phosphorus, vanadium, alkaline earths, and rare earths are not removed; their effect will be discussed later. No loss of aluminum was ever observed as a result of subjecting a solution to electrolysis in a mercury cathode cell.[6]

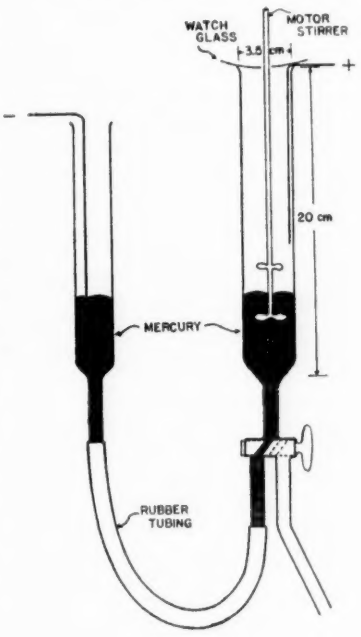

FIGURE 1.—*Modified mercury cathode cell.*

When contamination of the mercury by deposited metals reaches about 1 percent, further deposition is retarded, and the mercury should be cleaned.[7] Furthermore, if mercury which is too badly contaminated is used, there is danger that metals already deposited, will redissolve.

III. PROCEDURE

The range in which this method has been applied in this laboratory is from 0.02 to 0.08 mg of aluminum. All tests with the "aurin" reagent were made in a volume of from 40 to 75 ml, because after electrolysis in the mercury cathode cell the volume normally falls within these limits. However, if smaller volumes were used, the test would undoubtedly be applicable to amounts of aluminum below 0.02 mg.

Dissolve a convenient weight of sample in an appropriate acid.[8] Many nonferrous alloys can be dissolved in sulfuric acid directly, but

[6] For example, two determinations of aluminum in NBS Standard Sample Manganese Bronze 62, containing lead, copper, manganese, zinc, etc., in addition to 1.13 percent of aluminum, gave values of 1.12 and 1.14 percent by precipitation by ammonium hydroxide after preliminary mercury cathode separation. There is evidently no loss of aluminum even when the amount present is much greater than is ordinarily determined by the "aurin" method.

[7] The mercury is accumulated and 10 to 20 pounds cleaned at one time. It is cleaned well enough for further use as a cathode by covering it in a large thick-walled spherical flask with 10 times its volume of 10-percent nitric acid, and mixing vigorously by means of a jet of air or by suction until no further cloudiness or discoloration of the acid layer takes place. A water aspirator can be used. The flask is provided with a two-holed stopper. Through one hole a long tube leads to the bottom of the mercury; in the other hole a short tube leads to the aspirator. Depending upon the amount of contamination, 10 to 20 hours' mixing are required. Three portions of acid are usually sufficient, and about one-half of the mixing time should be devoted to the first portion.

[8] Throughout this paper whenever acids are mentioned, sulfuric acid will mean the concentrated acid of specific gravity 1.84; hydrochloric acid, the concentrated acid of specific gravity 1.18; and glacial acetic acid, the concentrated acid of approximately 99.5 percent. Ammonium hydroxide will mean the concentrated solution of specific gravity 0.90.

if another acid has been used, convert the sample to sulfate by gentle fuming with sulfuric acid.[9] Particular care must be taken to remove nitric acid completely. It is sometimes practicable to take an aliquot portion after the sample is dissolved and diluted to volume, and thus reduce the quantity of aluminum to within the proper range. In any case, the amount of sulfuric acid in the solution to be tested should be kept at a minimum, 5 ml or less. Dilute the solution to about 25 ml (too much dilution may cause tin and possibly antimony to hydrolyze), and filter off lead sulfate, if it is desired to reduce the length of time needed for electrolysis. Wash the filtrate into a mercury cathode cell (see fig. 1), if hydrolysis takes place disregard it, and electrolyze. When electrolysis is complete, separate the electrolyte from the mercury while at least part of the current is kept on. If the electrolyte contains floating particles of loose amalgam, it should be filtered. The volume of the solution should now be from 40 to 75 ml. Add 5 ml of hydrochloric acid, 5 ml of glacial acetic acid, and 5 ml of a 0.2-percent aqueous solution of a tested sample of ammonium aurintricarboxylate. Mix well while cautiously adding ammonium hydroxide [10] until the cloudy appearance of the dye disappears and the solution becomes clear, although still acid to litmus and still deeply colored. Place a piece of litmus paper against the inner surface of the beaker, and, while stirring constantly, add ammonium hydroxide at a rate of about 1 drop every 2 seconds until about 2 ml has been added; then add 1 drop every 3 or 4 seconds until the litmus paper turns blue. Now add 5 ml of glacial acetic acid, let the solution stand for 10 minutes, and neutralize it as previously described. Finally, add 5 ml of ammonium hydroxide. When the solution has cooled to room temperature, compare the color obtained with that of solutions of known aluminum content which have been similarly prepared. If the comparison is made in 150-ml beakers against a white background, a difference of 0.01 mg of aluminum can be readily distinguished.

IV. EXPERIMENTAL RESULTS AND DISCUSSION OF PROCEDURE

Although such observations as were made in this laboratory concerning the sensitivity of this method of determining aluminum, and of the effect of temperature, ripening period and excess of reagents, confirm the work of Yoe and Hill,[11] nevertheless the procedure which they proposed has the drawbacks mentioned earlier in this paper. In attempting to find the source of difficulty it was noticed that the rate of addition of ammonium hydroxide affected the results sharply. Two samples having the same aluminum content differed markedly when one was neutralized slowly and the other quickly. Duplicate samples sometimes differed even when ammonium hydroxide was added apparently at the same speed. It was noticed, however, that whenever a pair of these differing duplicates was reacidified with acetic acid, allowed to stand 10 to 15 minutes, and then neutralized again with ammonium hydroxide at any moderate rate, they "evened up" and did not fade subsequently. This observation formed the

[9] Just how much of any aluminum occurring as oxide is caught in this method is not known, for this would depend upon the solubility of the oxide in the dissolving acids. In any event, the total aluminum can be obtained by examining any residue left after decomposition of the sample.

[10] If the presence of rare earths or alkaline earths is suspected, ammonium hydroxide saturated with ammonium carbonate should be used throughout.

[11] J. Am. Chem. Soc. **49**, 2395 (1927).

basis for the modified procedure recommended in this paper. The reliability of the procedure as modified was confirmed by numerous tests with solutions which contained only the reagents involved and known amounts of aluminum. Since the method is designed for the determination of small quantities of aluminum, between the limits of 0.02 and 0.08 mg, the amounts of aluminum taken were 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, and 0.08 mg, respectively. By following the recommended procedure, the identical quantities of aluminum which had been added were again found. When no aluminum was added, no color was developed by the reagent.

Further experiments were made with five specimens of bronze which contained small quantities of aluminum. In this instance, the aluminum content was first determined gravimetrically in 5-g portions of the alloys. The percentages so obtained were 0.006, 0.018, 0.025, 0.03, and 0.05. The aluminum was then determined in the alloys according to the colorimetric procedure recommended in this paper. The results obtained were identical with those determined gravimetrically, and it is to be particularly noted that only 0.1 g of the alloy was required as a sample. To eliminate the personal equation, an additional operator independently repeated the colorimetric determinations, and obtained the same results as those given above.

To make certain that the aluminum in an alloy can be accurately determined by the recommended procedure, known quantities of aluminum were added to solutions of various types of alloys which either contained no aluminum or less than 0.001 percent, and subsequently recovered. The results of such experiments are given in table 1.

A comparison was also made of the recommended procedure with those of previous investigators. Unless the modified procedure as recommended in this paper was followed, erroneous results were obtained. For instance, a solution containing 0.05 mg of aluminum appeared to contain more aluminum than one to which 0.08 mg had been added, and a blank solution appeared to contain 0.03 mg of aluminum.

With the recommended procedure, no starch or other protective colloid is needed, and the time required to complete the determination, after removal of the electrolyzed solution from the mercury cathode cell, is from 20 to 30 minutes. The procedure has been successfully and satisfactorily applied for over 2 years to the routine determination of small amounts of aluminum in a large variety of nonferrous materials.

TABLE 1.—*Recovery of aluminum added to nonferrous alloys*

Material	Sample	Al added	Al found
	g	mg	mg
Antifriction metal; approx. composition: 63.7% Pb, 20.5% Sn, 14.0% Sb, 1.6% Cu	1.00	None	None
	1.00	0.03	0.03
	1.00	.05	.05
	1.00	.08	.08
Lead-base bearing metal No. 53; approx. composition: 79% Pb, 11% Sn, 10% Sb	1.00	None	<0.001
	0.50	0.10	[a].10
	.50	.10	.10
Solder; approx. composition: 50% Pb, 50% Sn	1	None	None
	3	None	None
	1	0.05	[a]0.05

[a] $PbSO_4$ filtered off before electrolysis.

V. REMOVAL OF INTERFERING SUBSTANCES

Fortunately, most of the elements likely to be contained in nonferrous materials which would interfere with the determination of aluminum by forming colored lakes or hydroxide precipitates are completely or nearly completely removed by a careful electrolysis of the solution in the mercury cathode cell. Hammett and Sottery [12] have contributed information of a qualitative nature as to the effect of some of the common and some of the less common elements that interfere. Corey and Rogers [13] and Middleton [14] contributed additional information concerning the less common elements. Although many of these latter elements are not ordinarily encountered in nonferrous work, some tests of their effect were made, mainly because it was suspected that the "aurin" reagent used in this laboratory may not have been the same as that used by other investigators.

1. BEHAVIOR OF ELEMENTS THAT CAN BE REMOVED BY MERCURY CATHODE TREATMENT

Of the list of elements given in section II of this paper as completely removable by electrolysis, only iron, copper, nickel, cobalt, zinc, gallium, germanium, thallium, silver, cadmium, indium, tin, antimony, chromium, molybdenum, lead, bismuth, arsenic, and mercury are likely to be encountered in nonferrous materials. Ordinarily, these will all have been removed before the "aurin" test is made, but failure to remove very small amounts is of consequence only in the case of iron. Iron must be completely removed because it gives a red color much like that produced by aluminum even when extremely small amounts of it are present. Mercury cathode treatment can be made to remove iron completely, but with samples of high iron content great care must be taken to wash down spray which carries iron up above the solution.

Gallium, indium, and thallium are closely related to aluminum and might be expected to interfere. Absence of other interfering elements may occasionally make it desirable to apply the test directly to solutions that have not been subjected to electrolysis in the mercury cathode cell. Tests were therefore made to obtain information concerning these elements in such solutions.

If the procedure is applied to a solution containing up to 0.10 mg of gallium by itself, there is no distinguishable difference in appearance between the blank and the solution under test, but larger amounts of gallium (2 mg) impart a deep red color to the solution. This interference can not be overcome by the use of ammonium carbonate solution.

Indium, in amounts up to 2 mg, does not interfere with the determination of small amounts of aluminum (0.05 mg), but larger amounts of indium (20 mg), even in the absence of aluminum, give a pink precipitate immediately upon completion of the test. Smaller amounts (10 mg) do not precipitate immediately, but if the solution is allowed to stand for 30 minutes, a pink precipitate may form. Ammonium carbonate has no effect on this precipitate.

Thallium, in amounts up to 2 mg, does not interfere with the determination of small amounts of aluminum (0.05 mg).

[12] J. Am. Chem. Soc. **47**, 142 (1925).
[13] J. Am. Chem. Soc. **48**, 2125 (1926).
[14] J. Am. Chem. Soc. **49**, 216 (1927).

2. BEHAVIOR OF ELEMENTS THAT CANNOT BE REMOVED BY MERCURY CATHODE TREATMENT

Beryllium interferes even in smallest amounts. It gives a color and sometimes a precipitate very similar to that of aluminum, and it therefore must be completely removed. Its separation can be effected with the help of a gathering agent that will in itself not interfere in the subsequent "aurin" test. Thus, a small amount of zirconium (about 40 times that of the aluminum present) as sulphate can be added to the solution containing aluminum and beryllium, and the zirconium and aluminum precipitated with 8-hydroxyquinoline according to the method described by Knowles.[15] Some tests made with this method showed that 2 mg of zirconium will safely gather and separate 0.05 mg of aluminum from 0.05 mg of beryllium. The resulting precipitate, which contains the aluminum and zirconium, is decomposed by nitric and sulfuric acids, gently fumed, and treated with "aurin."

Tests have shown that zirconium is without effect in amounts up to 10 mg, either in the presence or absence of aluminum, provided ammonium carbonate solution is used for neutralization. If ammonium hydroxide without ammonium carbonate is used, a copious red precipitate is formed.

Quadrivalent vanadium by itself (in amounts up to 2 mg) has no effect, but when as little as 0.0001 mg of aluminum is also present a deep color develops, which is soon followed by the formation of a precipitate. However, this precipitate dissolves, and the solution clears in about 15 minutes, leaving a clear blank color.

Quinquevalent vanadium (in amounts up to 1 mg) has no effect either in the presence or absence of aluminum, but larger amounts interfere by imparting a color to the solution.

Calcium, strontium, and barium (in amounts up to 10 mg) have no effect. The same amount of magnesium, however, gives a pink color somewhat similar to that produced by aluminum. This color is not discharged by the use of ammonium carbonate. In alloys containing appreciable amounts of magnesium, aluminum can be separated by twice precipitating with ammonium hydroxide after adding a suitable substance such as zirconium to "gather" the aluminum. The test is then made on the solution of this precipitate.

Scandium, lanthanum, and cerium form red precipitates which are promptly decolorized by ammonium carbonate solution.

Small amounts (1 mg) of uranium or titanium do not interfere, either in the presence or absence of aluminum, but larger amounts (10 mg) yield a slight reddish brown color.

Reasonable amounts of phosphoric acid (up to 25 mg) do not interfere with the test. Larger amounts bleach the color of the lake.

Nitric acid, sulfur dioxide, hydrogen sulfide, and hydrofluoric acid are all harmful to the test because they bleach the color of the lake. These are removed by the prescribed fuming with sulfuric acid.

WASHINGTON, March 15, 1938.

[15] J. Research NBS **15**, 87 (1935) RP813.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1118

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PREPARATION OF AMMONIUM AURINTRICARBOXYLATE

By John A. Scherrer and W. Harold Smith

ABSTRACT

A procedure is described for the preparation of an ammonium salt of aurintricarboxylic acid which is satisfactory for use in the colorimetric determination of aluminum. The development of this procedure was necessary because a sensitive reagent could neither be prepared by existing methods nor purchased in the market.

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I. INTRODUCTION

Thirteen years ago Hammett and Sattery [1] observed that the bright-red lake formed by aluminum salts and aurintricarboxylic acid is stable in an ammoniacal solution buffered with ammonium acetate, and that under these conditions the lake can be used as a test for aluminum. Upon this observation Lundell and Knowles [2] developed a quantitative method for the detection and determination of small amounts of aluminum in certain nonferrous materials. More recently Scherrer and Mogerman [3] utilized the reaction and applied the method to the determination of small amounts of aluminum in a variety of nonferrous materials.

The last-named authors found that a satisfactory reagent must show a definite pink color with 0.02 mg of aluminum in a volume of 50 ml, and only a slight straw color if aluminum is absent.

The reagent used by Lundell and Knowles, purchased in the market, happened to be satisfactory. When this lot was exhausted no product of similar quality could be obtained. Some of the preparations from more recent commercial sources were found to yield solutions which were unstable whereas others produced "muddy" precipitates. All of them were too deeply colored, in the absence of aluminum, to be satisfactory.

The preparation of the reagent, therefore, became necessary. A description of the method is given in this paper.

[1] J. Am. Chem. Soc. **47**, 142 (1925).
[2] Ind. Eng. Chem. **18**, 60 (1926).
[3] J. Research NBS **21**, 105 (1938) RP1117.

II. EXISTING PROCEDURES FOR PREPARING THE DYE

The dye was first mentioned in 1889 in a German patent [4] based on work by K. Sandmeyer. Directions were given for its preparation by the reaction of salicylic acid with formaldehyde in a mixture of concentrated sulfuric acid and sodium nitrite.

N. Caro [5] prepared aurintricarboxylic acid indirectly from 5, 5′-methylenedisalicylic acid, made by condensing formaldehyde and salicylic acid. To a mixture of 13 parts of concentrated sulfuric acid and 1 part of sodium nitrite was added a mixture of 2 parts of 5, 5′-methylenedisalicylic acid and 1 part of salicylic acid. The products of this reaction were poured into cold water, and the insoluble portion was removed by filtration. After repeated digestion and washing with hot water, the residue was dissolved in alkali and precipitated by hydrochloric acid. The product was then purified by a method which F. Zulkowsky [6] recommended for the removal of resins in the purification of aurin.

G. B. Heisig and W. M. Lauer [7] prepared the dye according to one of the methods described in the Geigy patent. To a quantity of sulfuric acid, cooled in an ice bath, sodium nitrite was added, with vigorous stirring, in small portions in order to suppress the evolution of oxides of nitrogen. Salicylic acid was then added slowly in small portions, and the mixture stirred at 20° C until all solid material was dissolved. The mixture was then surrounded by an ice-salt bath, and when the temperature reached 0° C formaldehyde was slowly added, with vigorous stirring, at such a rate that the temperature did not rise above 5° C. The reaction was said to be complete a few minutes after all the formaldehyde was added.

Apparently no explanation has been suggested for the reactions which occur when aurintricarboxylic acid is formed. Possibly a nitroso compound of salicylic acid is produced first, which, in its tautomeric form of a quinoneoxime, unites with 5,5′-methylenedisalicylic acid. The $=C=NOH$ (oxime) group is assumed to couple at the methylene linkage, and in so doing parts with nitrogen, hydrogen, and water in the proportions which are present in hydroxylamine.

Attempts to prepare the dye by the methods of Sandmeyer, Caro, and Heisig and Lauer yielded products unsatisfactory for use in the colorimetric determination of aluminum. The dyes were not very sensitive and "blank" determinations always showed a deep-yellow or orange color. It was observed that the reaction is not completed immediately after the addition of formaldehyde, and that more time than was usually allowed is necessary to form a dye of suitable characteristics. Further experimental work led to other refinements necessary to obtain a satisfactory product. The procedure, given in the following section, is based on that of Sandmeyer, but certain changes have been introduced with respect to temperature, time of reaction, and washing treatment.

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[4] D. R. P. 49970, issued to Joh. Rud. Geigy and Co.
[5] Ber. deutsch. chem. Ges. **25,** 941 (1892).
[6] Am. Chem. Pharm. **202,** 200 (1880).
[7] Organic Syntheses **9,** 8 (1929).

III. RECOMMENDED PROCEDURE

The following procedure was found to produce ammonium aurintricarboxylate suitable for use in the determination of small amounts of aluminum.

Add 4 g of sodium nitrite, in small portions and while vigorously stirring, to 44 ml of sulfuric acid (sp gr 1.84) contained in a 250-ml beaker. The nitrite should be added slowly to prevent excessive evolution of oxides of nitrogen. When all of the nitrite is dissolved, cool the solution to 10° C. Over a period of 5 to 10 minutes, next add 12 g of salicylic acid, while again stiring the solution. Cool the solution to 3° C by immersing the beaker in crushed ice, and add dropwise 3.5 ml of an approximately 37-percent solution of formaldehyde, while again vigorously stirring. Since the temperature at this stage must not exceed 5° C a small thermometer makes a convenient stirrer. When all the aldehyde has been added, allow the beaker to remain in the ice bath for about 1 hour and stir the contents every 5 minutes. The reaction is now allowed to proceed at a reduced temperature for about 20 hours. A cooling bath is conveniently made by placing a 20-lb block of ice in a tray having approximately the dimensions 12 by 12 by 3.5 inches and filling the tray with ice water. With this arrangement, when the room temperature is 20 to 25° C, the temperature of the reacting mixture will increase about 1 to 2° C during the first 7 hours and then gradually to about 20° C during the next 13 hours.

Cover the beaker containing the reacting mixture, place it in one corner of the tray, and weight it to prevent tipping. Allow the beaker to remain in the ice bath for 20 hours. At the end of this time, slowly pour the contents of the beaker into 2 liters of cold distilled water, while constantly stirring. When the solution has stood for 1 hour, filter it, using a Büchner funnel and a 15-cm paper of close texture. Wash the precipitate three times with distilled water and then return it to the beaker in which the precipitation was made. Add 1 liter of water and 50 ml of hydrochloric acid (sp gr 1.18), and boil for 2 or 3 minutes. Let the precipitate settle for 10 minutes and then wash it three times by decantation with water. Crush and break up the black mass with a stirring rod which has been flattened on one end. Repeat the boiling treatment with 1 liter of water and 50 ml of hydrochloric acid, as well as the subsequent washing with water, twice more.

Finally, dissolve the residual mass in an excess of ammonium hydroxide, and evaporate the resulting solution to dryness on the steam bath. Grind the cooled residue to a fine powder, and transfer to a bottle.

WASHINGTON, May 17, 1938.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1119

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COMBINATION OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE WITH HIDE, TENDON, AND BONE COLLAGEN

By John Beek, Jr.

ABSTRACT

The amounts of hydrochloric acid and sodium hydroxide combining with three different samples of collagen were measured. The samples of collagen were prepared from the tissues of hide, tendon, and bone. The three materials combine with substantially the same amounts of acid, but the bone collagen combines with a larger amount of base than do the other two. This difference is explained by the loss of amide nitrogen during the preliminary treatment of the bone collagen, which indicates that the collagenous substances of the three natural tissues are identical.

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I. INTRODUCTION

An investigation of the nature of quinone tanning is in progress in this laboratory. As a part of the program of this investigation, some of the chemical properties of collagens from different tissues are being compared, with the object of obtaining evidence bearing on the question of the chemical individuality of white fibrous connective tissue. It is also proposed to compare the acidic and basic properties of collagen and quinone-tanned leather. This paper is a report of the work on the acidic and basic properties of samples of collagen prepared from the hide, tendons, and bones of a steer.

The reactions of collagen and gelatin with acids and bases have been studied by a large number of workers. A survey of the literature led to the conclusion that the best basis for comparing the amounts of acid or base combining with different samples of collagen would be obtained by measuring the quantity of acid or base taken up from an aqueous solution containing a high concentration of salt. Theoretically the use of a nonaqueous solvent or a gaseous acid or base would give more accurate results, but the inconvenience of making the corresponding measurements was considered prohibitive. For

example, the difficulty of eliminating water from such a system is considerable, and yet if any significant quantity of water is present the measurement becomes inaccurate.

II. THEORY OF THE MEASUREMENT

There are four conspicuous difficulties in the interpretation of the change in the concentration of an aqueous solution of an acid or base, brought about by the introduction of an insoluble protein.

First, there is the essential weakness of the measurement of adsorption from solution, resulting from the relative nature of the measurement. The only quantity that can be determined is a function of the amounts of the two components adsorbed and the equilibrium concentration of the solution. A third component may be added to the solution and used as a reference substance in calculating the amount of adsorption, but the calculation still depends on the assumption that the new substance is not adsorbed, and there is the further disadvantage, for the general case, that the nature of the system is changed. However, in the case of the system collagen-hydrochloric acid-sodium chloride-water, with the acid dilute and the salt approaching saturation, it has been shown [1] [1] that the amount of adsorption calculated with reference to the water is in agreement with that calculated with reference to the salt. Here no disadvantage arises from the presence of the salt, as it could not be expected to change the combining weight of the collagen.

Second, there is the uncertainty arising from the fact that a considerable quantity of solution passes into the protein phase. As the ratio of uncombined acid or base to uncombined water can not be directly determined in this part of the solution, any calculation of the total amount of uncombined acid or base in the system must depend on some assumption about the activity coefficients of the ions in the protein phase. For instance, in the system given in the preceding paragraph, the calculation of the amount of acid removed from solution, using the salt as reference substance, depends not only on the assumption that no salt is removed from the solution, but also on the assumption that the fractional change in the activity coefficient on passing from one phase to the other is the same for acid and for salt.

Third, there is the error introduced by the change of a part of the insoluble protein to a soluble protein, through the action of the acid or base. In the case of collagen, this effect has especial importance when alkaline solutions are used. In order to correct for the effect of the dissolved matter, it is necessary to make sure in the titration that all the acid or base in the solution is neutralized, whether or not it was combined with dissolved protein in the solution at equilibrium. Then, to calculate the specific adsorption for the solid protein, it is only necessary to consider the distribution of the total acid or base in the system between the part in solution (whether combined or not) and the part combined with the remaining solid protein. Of course, if the protein is completely dispersed, the calculated adsorption becomes indeterminate and the method fails.

The effectiveness of this method was tested experimentally by carrying out four measurements of the adsorption of sodium hydroxide by hide collagen in solutions about 0.08 molal in base, allowing the systems to stand for periods of 1, 2, 4, and 8 days. In this way the

[1] Numbers in brackets indicate literature references at the end of this paper.

fraction of the total nitrogen in solution was varied from 11 to 26 percent. The difference between the extreme values of the calculated adsorption was less than 4 percent, and the order of the determinations with reference to the amount of adsorption was not the same as the order with reference to the amount of collagen dissolved. These results indicate that this method of correcting for the effect of the dissolved matter is satisfactory.

Fourth, there is the problem of determining the amount of acid or base that is introduced as an impurity with the protein. The custom of experimenters in this field has been to dispose of the question by assuming either that the material as prepared contains no acid or base, or that the isoelectric point of the protein, as indicated by measurements of its electrophoretic mobility, corresponds to the condition in which the amounts of acid and base combined are equivalent. In the present work the amount of acid present in the collagen was measured directly. This was possible because the only acidic or basic substances used in processing [5] the collagen were calcium carbonate, calcium hydroxide and hydrochloric acid, so that the difference between the amounts of chloride and calcium present (expressed in equivalents) gave the acid content directly.

The assumption that the neutral point and the electrophoretically determined isoelectric point of collagen are identical was tested by putting a 5-g sample of hide collagen in 100 ml of water containing just enough sodium hydroxide to neutralize the acid in the collagen, and measuring the pH of the solution with the glass electrode. A period of 4 days was allowed for the system to come to equilibrium. The pH of the solution at the end of this time was 7.7. This result is consistent with the fact that collagen contains more basic groups than acidic groups. Also, it affords a simple explanation of the pronounced end point in the titration curve of collagen [3, 4] between the pH values of 7 and 10. As electrophoretic measurements give a value of about 5 for the isoelectric point [2, 10], it may be concluded that the assumption in question is not valid for collagen, and thus can not be valid in general.

III. PREPARATION OF COLLAGEN

The raw materials from which the samples of collagen were prepared were obtained, through the courtesy of the U. S. Department of Agriculture, from a steer slaughtered at the Experimental Station at Beltsville, Md. The bend portion of the hide, the carpal and tarsal flexor tendons, and the metacarpal and metatarsal bones were used.

With certain exceptions, as noted below, the materials were processed according to the method given by Highberger [5]. The tendons were prepared for the treatment with trypsin by cutting away all muscular tissue and removing as much as possible of the areolar connective tissue from the outside. They were then cut into sections about 1 cm in length. The bones required more drastic preliminary treatment. The ends were cut off, the marrow was removed, and the periosteum was scraped off. They were then put into a 0.1 *N* solution of hydrochloric acid, covered with a layer of xylene. The solution was changed every day or two for a month, and after this twice a week for three more months. At the end of this time the material was cut into small pieces, and further washed with dilute hydrochloric acid until no opaque regions remained. The effect of

this long treatment with acid appeared when the amount of the material dissolving in alkaline solutions was determined. A much larger quantity of nitrogen was found in solution with the bone collagen than with either the hide or tendon. Hydrochloric acid was used for the final removal of calcium from all three materials.

The purified materials were analyzed for chlorine and calcium. The chlorine contents of the samples, expressed as the ratio of the number of gram-atoms of chlorine to the number of gram-atoms of nitrogen in the sample, were 0.0048, 0.0005, and 0.0044 for the hide, tendon, and bone, respectively. The calcium contents of all the samples were less than 0.0002, expressed in the same way. A qualitative test for phosphate in the bone collagen gave a negative result. The ash content of the hide collagen (determined after adding sulfuric acid) was 0.05 percent.

IV. EXPERIMENTAL PROCEDURE

The samples of collagen were conditioned and weighed in an atmosphere at 65-percent relative humidity and 22° C 0.97 g of collagen, 20 ml of hydrochloric acid or sodium hydroxide solution of the desired concentration, and an excess of solid sodium chloride were put in a glass-stoppered flask. The flask was put in a constant-temperature room at 25° C and allowed to remain, with occasional shaking, for 25 hours. Part of the solution was then poured into a test tube, the tube was stoppered, and the suspended solid matter was allowed to settle. After settling, a 10-ml sample of solution was pipetted into a flask for titration. The titration was carried out volumetrically with 0.05 *N* sodium hydroxide or hydrochloric acid, using methyl red as the indicator. The titration was run past the exact end point of the indicator, as it was necessary, for the reason given above, to neutralize all the acid or base in the solution, without regard to its combination with dissolved matter from the collagen. Finally, the total nitrogen in the solutions titrated was determined.

V. CALCULATION OF RESULTS

The mass of water in a unit volume of a saturated aqueous solution of sodium chloride containing a small amount of hydrochloric acid or sodium hydroxide is practically independent of the concentration of acid or base [6, 7, 8, 9], and is equal to 0.882 g/ml at 25° C. In this work the effect of the dissolved nitrogenous matter on the concentration of water was neglected.

The total mass of water in the system was taken as 0.03 g less than the mass of water added. This difference represents the amount of water taken up by the collagen in passing from 65- to 75-percent relative humidity. This correction was made because the collagen used in the work cited above [1] was conditioned at the higher humidity.

The fundamental equation used for calculating the results was $A=f\left(N-H\frac{n}{h}\right)+H\frac{a}{h}$, where A is the total acid or base in the system (including that introduced with the collagen), N is the total nitrogen, H is the total mass of water, and f is the desired ratio of acid or base fixed to undissolved nitrogen. The lower-case letters refer to the amounts of the same components in the part of the system taken for

titration. A and N are expressed in equivalents. This equation expresses the fact that the total acid or base is the sum of that part fixed by the undissolved collagen, and the part in solution. The ratio f is thus given in the symmetrical form

$$f=\frac{A-H\frac{a}{h}}{N-H\frac{n}{h}}.$$

The equilibrium concentration was calculated under the assumption that the ratio of combined acid or base to nitrogen was the same for the dissolved and undissolved portions. There is no assurance that this is a good approximation, but the concordance of the results indicates that the concentration calculated in this way is satisfactory for use as an independent variable in presenting the results. The molal concentration of acid or base was calculated from the expression $m=(A-fN)/H$.

VI. DISCUSSION OF RESULTS

The experimental results are given in tables 1 and 2, and in figure 1.

TABLE 1.—*Combination of collagen with hydrochloric acid*

[m is the molal concentration of acid in the equilibrium solution. f is the ratio of the number of equivalents of acid combined to the number of equivalents of nitrogen in the sample.]

Hide		Tendon		Bone	
m	f	m	f	m	f
0.002	0.070	0.004	0.074	0.005	0.072
.006	.071	.017	.077	.018	.074
.011	.073	.039	.080	.039	.079
.016	.074	.064	.085	.066	.082
.022	.075	.098	.092	.100	.088
.030	.076				
.039	.079				
.051	.080				
.066	.083				
.088	.088				

TABLE 2.—*Combination of collagen with sodium hydroxide*

[m is the molal concentration of base in the equilibrium solution. f is the ratio of the number of equivalents of base combined to the number of equivalents of nitrogen in the sample.]

Hide		Tendon		Bone	
m	f	m	f	m	f
0.002	0.010	0.005	0.022	0.003	0.025
.003	.016	.017	.028	.014	.034
.006	.020	.038	.030	.034	.039
.010	.023	.064	.032	.060	.041
.015	.025	.098	.033	.091	.047
.022	.027				
.031	.027				
.042	.029				
.056	.029				
.074	.030				

Perhaps the most noticeable thing in figure 1 is the difference between the results for the bone collagen and those for the other two materials in the alkaline solutions. It is natural to look for the source of this difference in the treatment used for deliming the bones. There is no reason to suppose that peptide linkages were hydrolyzed by the long treatment with acid, because the amount of acid combined is the same for the bone as for the hide and tendon. If unsubstituted amide groups were hydrolyzed, however, the amount of base bound would increase without any change in the combining weight with respect to acid. A comparison of the amounts of ammonia nitrogen

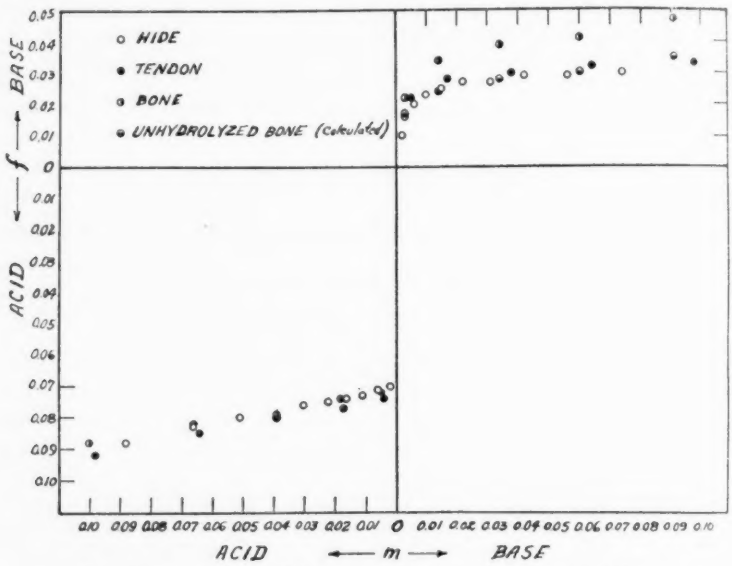

FIGURE 1.—*The combination of collagen with acid and base.*

The abscissas represent the molal concentrations of hydrochloric acid or sodium hydroxide. The ordinates represent the amounts of acid or base combined, expressed as the ratio of the number of equivalents combined to the number of equivalents of nitrogen in the sample.

in acid hydrolysates of the hide and bone collagens showed that the fraction of the total nitrogen as amide nitrogen was less by 0.010 in the bone collagen.

It is possible to calculate approximately what the amount of base combined with the bone collagen would have been if carboxyl groups equivalent to this amount of nitrogen were replaced by amide groups, assuming that the fraction of the number of carboxyl groups present which react with the base is a function only of the concentration of base. It appears from figure 1 that the carboxyl groups in the collagen are almost completely neutralized even at low concentrations of base, and that additional base is taken up by some noncarboxylic groups. The amount of this additional base combined seems to vary

nearly linearly with the concentration, in the range of concentrations covered. The calculation in question was made on the basis of these observations. The constants in the linear relation between f and m for the bone collagen were evaluated by the method of least squares, using the three highest values of m and neglecting the errors in m. If the four highest values of m are used the results are practically the same. The only object in using the method of least squares here was to make the calculation as nearly objective as possible. The constant term in the equation giving f as a function of m ($f=0.033+0.15\,m$) was taken to represent the limiting amount of base combining with carboxyl groups, the first degree term to represent the additional amount of base combined. Then, if 0.010 (the difference in the fraction of the total nitrogen as amide in the bone and hide collagens) is subtracted from the constant term, the difference is the calculated value of the limiting amount of base combined with carboxyl groups, for the modified bone collagen. The ratio of this difference to the constant term, $(0.033-0.010)/0.033$, gives the factor for converting the amount of base combined with carboxyl groups in the bone collagen to the amount for the modified bone collagen. Then the calculated f is given by the expression

$$\frac{0.023}{0.033}(f-0.15\,m)+0.15\,m.$$

Figure 1 shows the comparison of these calculated values with the observed values for the hide and tendon. It may be seen that the difference between the amide nitrogen contents accounts for the difference between the amounts of base combined. It seems proper, therefore, to conclude that the white fibrous connective tissues of hide, tendon, and bone behave alike with respect to combination with acid and base, and that the drastic treatment with acid hydrolyzed a considerable fraction of the amide groups in the bone collagen.

VII. SUMMARY

Collagen from three different sources, hide, tendon, and bone, was purified by the method given by Highberger [5]. The amounts of hydrochloric acid and sodium hydroxide taken up by these materials from dilute solutions of acid or base, saturated with sodium chloride, were measured. Four of the possible sources of error in the measurement are discussed, and the methods used for overcoming them, or the assumptions involved in disregarding them, are outlined. The pH of a solution in equilibrium with neutral hide collagen is found to be in the neighborhood of 8. The three samples of collagen are found to combine with equal amounts of acid, but the bone collagen combines with more base than do the other two. This difference is accounted for by a loss of amide nitrogen during the preliminary treatment of the bone collagen. It is concluded that the white fibrous connective tissues from the three sources exhibit the same behavior toward acids or bases.

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WASHINGTON, March 23, 1938.

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